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SLONAKER, Jr., Robert Evan, 1923-
FACTORS AFFECTING THE GROWTH AND THE
MECHANICAL AND PHYSICAL PROPERTIES OF
BISMUTH SINGLE CRYSTALS.

Iowa State University of Science and Technology
Ph.D., 1964
Engineering, chemical

University Microfilms, Inc., Ann Arbor, Michigan

FACTORS AFFECTING THE GROWTH AND THE MECHANICAL
AND PHYSICAL PROPERTIES OF BISMUTH SINGLE CRYSTALS

by

Robert Evan Slonaker, Jr.

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Chemical Engineering

Approved:

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Ames, Iowa

1964

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INTRODUCTION

The growing of single crystals has taken on new significance as a result of current and proposed needs of research groups and industry. Metallurgists and physicists have been intensifying their investigations into the properties of materials that exist in the crystalline form at normal atmospheric temperatures and pressures. Many of these studies have involved the use of single crystals; the materials most frequently considered have been the metals. The present commercial applications of semiconductors are a result of earlier solid state research.

One forecast (14) concerning the types of engineering materials to be found in the future includes brittle single crystals composed of interstitial compounds of transition metals or covalent compounds of light elements. The strength estimated for these materials is in the million-psi range, or roughly ten times that of present steels. A lack of plastic flow in these materials is expected to present difficult but not insurmountable design problems. The interesting feature of the article is that single crystals are spoken of as having practical engineering applications other than as research specimens or electronic components.

In recent years, significant advances have been made in the development of methods for obtaining ultra-high-purity metals. The availability of these materials, along with

reasonably dependable techniques for growing single crystals, has permitted further investigation into the true nature of metallic solids. Certainly, the higher the metal purity and the more perfect the single crystal, the closer the investigator comes to working with the basic unit of the usual polycrystalline solid. Also, the impurity content of semiconductors has been decreased to a point where the behavior of these materials in practice has become even more predictable.

Single crystals used for research purposes often need to be as physically perfect as possible and should be of a convenient size and shape. The choice of method for growing the crystal will depend mainly upon the physical properties of the compound or element involved but also upon the subsequent treatment or use for which the crystal is intended; and, of course, for a commercial operation, the choice would be the optimum process economically. It would be ideal to have a constant inter-relationship between the possible variables in a given process and the perfection of the resultant single crystals. However, since conditions necessarily change with the type of crystals being grown it is usually true that no simple correlations exist that will hold for all materials; and techniques must be modified, to some extent at least, with a change in the material. It is with these crystal growing processes, therefore, that some study is necessary to determine their capabilities and their limitations and in every case to attempt to make crystal growing more of a science.

In this investigation, single crystals of bismuth were grown under various sets of conditions, and several characteristics of these crystals were then determined. Bismuth was chosen as the material to be investigated because of interest developed during some preliminary studies with this material. Also, bismuth has a relatively low melting point, is not too reactive chemically, and possesses the interesting feature of undergoing expansion during solidification.

The Bridgman technique was chosen as the crystallization method because of its ready applicability to producing single crystals of low-melting materials. Also, shaped samples were desired for tensile tests on some of the single crystals, and it was felt that the Bridgman technique provided the best means of obtaining such crystals directly.

The purpose of the investigation was to study the factors affecting the growth of bismuth single crystals by the Bridgman method as well as to ascertain some of the variables influencing the mechanical and physical properties of these crystals.

PREVIOUS WORK

Growth of Single Crystals

General theory

Lawson and Nielsen (23) provided a brief but excellent survey of current crystal growing techniques including descriptions of typical apparatus required in each instance. The authors classified these methods under (a) growth from the melt, (b) growth from the vapor, (c) growth from supersaturated solutions, (d) growth by electrodeposition, (e) growth by thermal diffusion and (f) growth by "other methods," such as Verneuil's flame fusion method. Davis and Batteau (10), in their paper concerned with the growth of metal single crystals, spoke also of a strain anneal technique in the solid state which could be considered as a type of thermal diffusion process. For the purpose of this study, the methods of growth from the melt will be emphasized since most of the common techniques for growing pure metals and compounds fall into this category.

In pure metals or compounds, with little or no impurity present, the latent heat of solidification opposes formation of a nucleus unless the heat can be taken up by a foreign particle, by the walls of the crucible, or through supercooling. Holloman and Turnbull (17) have shown that the amount of supercooling is inversely related to the volume of the melt. Also, the melt apparently acts like a supersatu-

rated solution. That is, during supercooling, any disturbance, such as vibration of the melt or the addition of an impurity or other seed, can initiate solidification.

Buckley (5) discussed several additional natural phenomena encountered in any attempt to grow a single crystal directly from a melt with no seed crystal present initially. Included among these were the effects of the cooling rate during solidification and the factors affecting the lattice orientation of the resulting crystal.

As the melt cools to its freezing point and below, nuclei of the solid phase eventually form, and growth takes place on each nucleus individually. If the melt has been cooled rapidly, a relatively large number of nuclei form; a slower rate of cooling yields fewer nuclei. In the case of a freezing metal, these growing, solid particles are individual crystals, all with the same crystal structure but each oriented completely at random with respect to neighboring crystals in the remaining melt.

If a single crystal seed of the compound or metal were placed in contact with the surface of the melt and a proper temperature gradient established, solidification of the melt could be made to be influenced by the crystal structure of the seed and its lattice orientation. Czochralski (9) was one of the originators of the "crystal pulling" technique which uses these principles and which has been used to produce single crystals of many materials. Zone melting techniques, as

developed originally by Pfann (33), have also been used for growing large single crystals from a single crystal seed.

The Bridgman technique

If the liquid-solid transformation described above is considered in the light of an attempt to grow a single crystal directly from the melt, it can be seen that one nucleus must be formed and encouraged to the exclusion of all other possible nuclei. Tammann (41) combined a slow cooling rate and a crystallizing tube, which was tapered down to capillary size at the lower end, in an attempt to minimize the number of seed nuclei formed at the tip. Then, since heat was being extracted through the tip and since crystal growth is anisotropic, nuclei with the proper orientation grew most rapidly and tended to dominate the solidification of the melt. If a single crystal emerged upward from the capillary and the cooling rate were carefully controlled, a large single crystal could be obtained. Obreimov and Schubnikov (30) carried out a similar, classical work.

The Bridgman method (4) actually used the same general principles followed by Tammann and by Obreimov and Schubnikov. However, cooling was accomplished by lowering the crystallizing crucible or tube from the furnace where melting occurred into cooler surroundings. In the classical Bridgman method as in more recent variations, crystallization begins at the tip of the crystallizing tube or crucible. A single

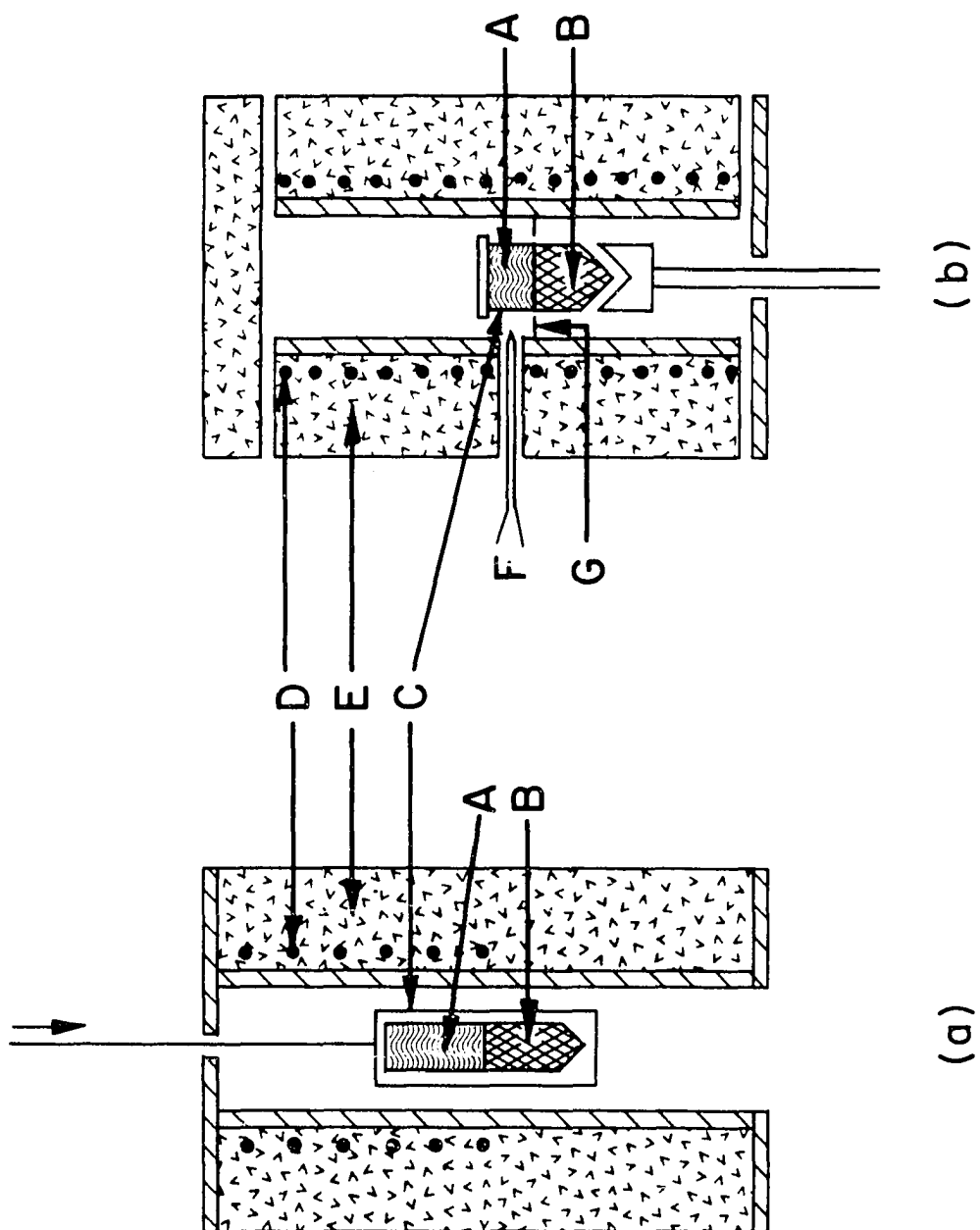
crystal seed is chosen either by so-called "natural selection," if a conical crucible tip is used, or through the action of a constriction or a capillary at the tip. Heat should be removed through the bottom of the crystal with apparatus design and lowering rate such that the minimum amount of cooling occurs from the sides of the crucible.

The Bridgman principle has been used by Kapitza (20) to grow single crystals of low melting point materials such as bismuth and by Quimby (34) to grow single crystals of high melting point materials such as nickel. In a modification of the basic Bridgman technique, Stockbarger (40) used two separate furnaces with the temperature of one held above and the temperature of the other held below the melting point of the material being crystallized. Stockbarger grew single crystals of calcium fluoride and lithium fluoride. The Bridgman unit and the Stockbarger unit are shown schematically in Figure 1.

Noggle (29) has described a method for growing shaped single crystals of aluminum in a "soft mold" of alumina contained in a vacuum retort. In this technique a polycrystalline specimen, machined to shape, was placed in a crucible, imbedded in alumina, and then melted and recrystallized as a single crystal using the Bridgman technique. Sosin and Koehler (39) in extending this procedure, cast potential probes into place in shaped aluminum tensile test specimens and found the resulting single crystals satisfactory for determining an electrical resistivity tensor for aluminum. As

Figure 1. Single crystal growth (a) Bridgman method (4)
 (b) Stockbarger method (40)

Legend: A - melt
 B - solid
 C - crucible
 D - furnace windings
 E - thermal insulation
 F - thermocouple
 G - radiation shield



a part of this thesis, similar work was done with bismuth. Portions of this data have already been published (36).

A version of the Bridgman method has been used by Olson (31) to grow single crystals of zinc, lead, tin and silver chloride and by Long (25) to grow single crystals of bismuth. The latter investigator also used a "soft mold" of alundum powder such as previously described to minimize the effect of the expansion of bismuth during solidification. In a similar but larger unit than that used in the latter two studies it was shown that large single crystals of zinc, 2-1/4 in. in diameter by 7-1/4 in. in length, could be grown in graphite crucibles by this method; and that, by using the same operating conditions, it was possible to grow seven single crystals of zinc, 3/8 in. in diameter by 7-3/8 in. in length, simultaneously (37).

Buckley (5) and Lawson and Nielsen (23) offer other illustrations of the use of the Bridgman method. The Bridgman-type units can be adapted for use with a vacuum or with controlled atmospheres. Some modifications have involved horizontal arrangements (7). The main, general advantage of the method is the ability to grow specimens of any reasonable shape and dimension. A significant disadvantage is the fact that generally the crucible or containing element is opaque, and no visual control of the process is possible.

Characteristics of Single Crystals

Single crystals versus polycrystalline materials

The mechanical properties of many metals and alloys have been reported in the literature. Shear and tension moduli, tensile and yield strength data all become available almost as soon as an alloy is put on the market. However, few engineers realize that such information consists of approximations, and that the true properties can only be found by studying single crystals of the material.

It is reasonable to assume that the properties of the aggregate are some function of the properties of the individual crystals making up the aggregate. However, Sinnott (35) reminded us that the function relating the two evidently is not a simple one since the mechanical properties of single crystals are different from those for the aggregate of the same material by several orders of magnitude. The difference in physical properties, such as electrical and magnetic properties, is not as pronounced since these properties are not so structure-sensitive. However, both the mechanical and the physical properties are affected at least to some extent by the perfection of the crystal or crystals involved.

Imperfections in crystals

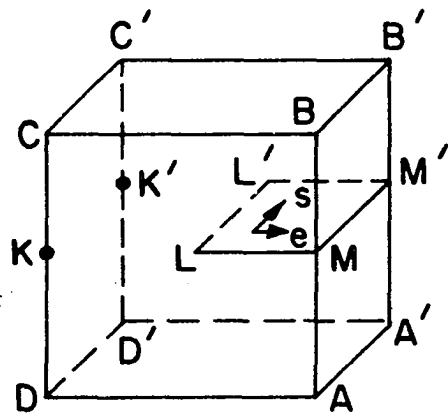
The usual object in growing single crystals is to grow as perfect a representation of the atomic arrangement of a given solid as is possible. Whether the crystal is for research

purposes or for commercial use, as, for example, an electronic component, a perfect crystal is most desirable. However, because of the large probability that defects will occur, the producer should be prepared to define in some way the relative perfection of his product.

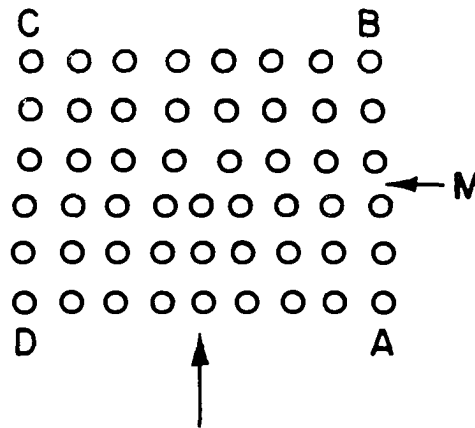
Jaswon referred in survey form to the imperfections in "nearly perfect" crystals (19). The imperfections mentioned included dislocations, stacking faults, and point defects. This was a general classification and perhaps includes the defects most important in single crystal studies. However, the investigator should not (and frequently cannot) neglect the presence of phonons, or lattice vibrations, and of surfaces. In the case of single crystals, the latter include only the crystal surface and any subgrain boundaries that might develop within the growing crystal.

Dislocations Dislocations serve as a means of helping to explain plastic deformation in crystalline materials. The dislocation theory is primarily one of lattice defects, and seems applicable to most phenomena noticed in metals.

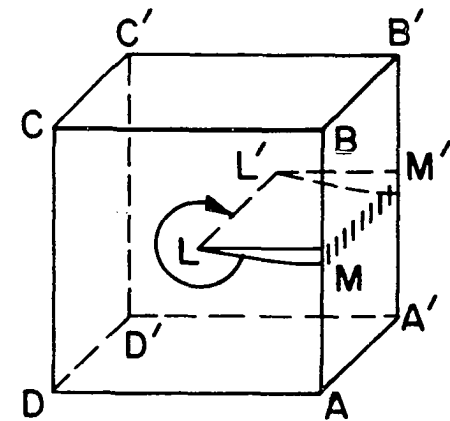
Two types of dislocations have been recognized: edge and screw. The edge dislocations appear when a plane of atoms is removed or displaced in a lattice. A screw dislocation can be defined when a crystal is made up not of parallel planes of atoms, one above the other, but of a continuous plane in the form of a helicoid (35). Figure 2 illustrates the difference between these two phenomena. If the cube in Figure 2(a) is cut



(a)



(b)



(c)

Figure 2. Construction of dislocations (2)
 (a) edge dislocation (b) plane of atoms showing edge
 dislocation (c) screw dislocation

on a plane LL'MM' and if the remainder of the plane between KK' and LL' is rigidly fixed, a movement of the block above LL'MM' can be made an integral number of interatomic distances parallel to LM and L'M' in such a manner that the atoms in plane ABCD will appear as in Figure 2(b) after the distortion has been distributed evenly on both sides of LL'. This is an edge dislocation as compared with a screw dislocation which is formed by movement of the crystal sections above and below the cut in a direction parallel to LL' and MM'. The latter defect is shown in Figure 2(c).

The origins of dislocations are perhaps not definitely known. Bennett and Sawyer (1), in their paper on the production of single crystals of germanium by zone leveling, speculated that dislocations may be produced, in germanium at least, by three mechanisms: propagation from the seed into the new lattice as it grows, the result of possible growth faults, and the plastic deformation of the solid crystal. These three influences may be minimized, respectively, by using the best available seed, by using slow growth rates, and by minimizing stresses on the crystal. The influence of plastic deformation of the crystal was thought to be the most important. Kurtz, Kulin and Averbach (22) confirmed the influence of growth rate on the characteristics of germanium single crystals. These authors stated that above a growth rate of 0.15 in./min. the dislocation density increases rapidly and varies with growth direction. They felt that high

growth rates either prevent the segregation of impurity atoms at dislocations or lead to extensive dislocation clustering.

The effect of dislocations on strength properties is interesting. The crystal will be extremely strong if no dislocations exist within it (witness single crystal whiskers with strengths approaching the theoretical strength for the material). If one dislocation is introduced, the material loses much of its strength. As more dislocations are introduced, the material will grow still weaker until the dislocation content increases to a point where mutual interaction of the dislocations causes the strength to increase again.

Stacking faults Stacking faults are defined as being deviations from the normal stacking sequence of atoms as found in crystals. Specifically, referring to Figure 3, the A layer of spheres represents a close-packed layer of atoms. The next layer packed on top could be located at either the B or C positions. A third layer of spheres laid on top could then be placed at either the A or C or the A or B positions respectively. The ABCABC packing sequence is to be found in the face-centered cubic crystals; the ABABAB sequence represents the packing found in the close-packed hexagonal lattice. Any irregularity in packing in either sequence becomes a stacking fault; and these faults are closely related to the dislocations in a crystal.

Point defects Point defects include impurity atoms on lattice sites, vacant lattice sites, interstitial atoms, or a

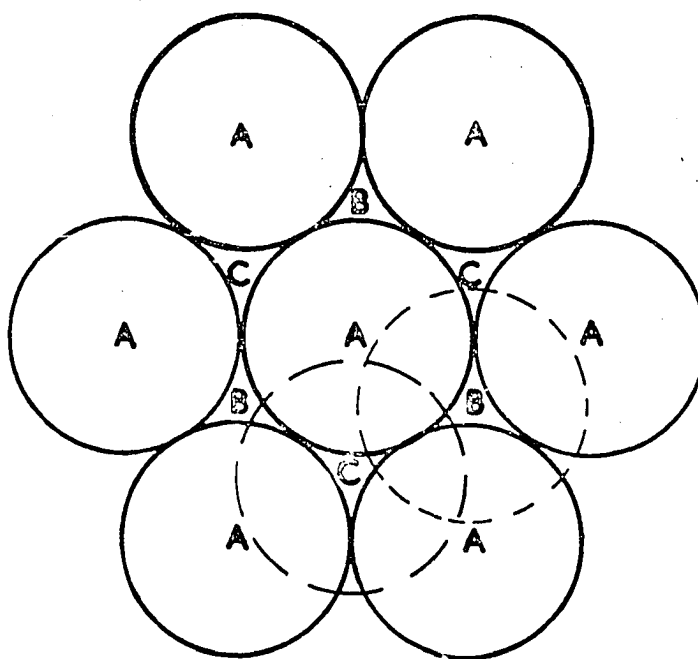


Figure 3. Spheres packed in a close-packed array
(letters denote possible sites for sphere centers)

combination of the latter two conditions called a Frenkel defect. Figure 4 illustrates the Frenkel defect and the Schottky defect, the latter consisting only of vacancies.

In a pure metal crystal, vacancies become the most effective type of point defect. Jaswon (19) related the equilibrium concentration of vacancies to temperature by the relationship:

$$C \propto e^{-W/kT}$$

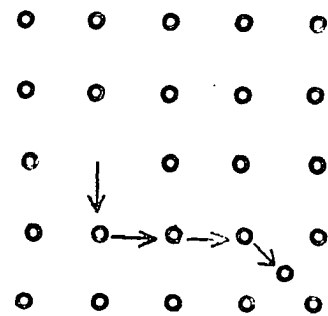
where: C = fraction of vacant sites
at equilibrium

W = energy required to move atom
from interior of crystal to
the boundary

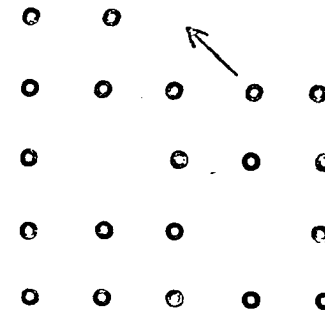
k = Boltzmann constant

T = absolute temperature

The author reported a value of W equal to about one electron volt for copper, a value sufficiently low to cause a vacancy concentration of 10^{-6} at room temperature. In general, these considerations apply to dislocations also, but the activation energy is so high that no dislocation is formed as a result of thermal energy requirements. Conversely, therefore, a dislocation is thermally stable and will persist indefinitely unless it is cancelled by other dislocations or by condensation of point defects or unless it is removed by exit at a free surface.



(a)



(b)

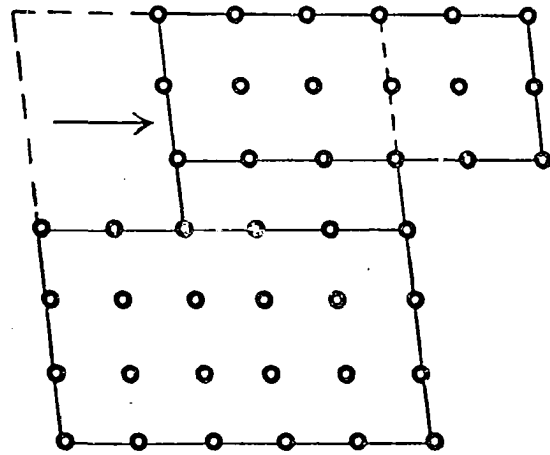
Figure 4. Point defects in a crystal of pure metal (8)
 (a) Frenkel defect (b) Schottky defect

Mechanical properties

Mechanical or strength properties are known to be structure-sensitive. During appropriate tests with single crystals it soon becomes apparent not only that no simple theory of elasticity would apply to all types of crystals but also that their behavior during plastic deformation differs markedly from that of a polycrystalline aggregate of the same material. Two main factors are exerting their influence in these instances: the differences in bond strengths between the different materials and the inherent anisotropy in properties exhibited by single crystals.

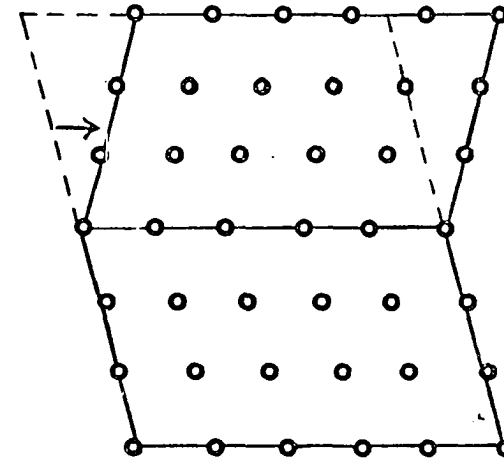
Deformation mechanisms When a crystal is undergoing deformation, there are several ways that it may yield to lessen the applied stress. The deformation mechanisms include slip and twinning, which have been theorized as the low temperature processes, and creep, which is important at high temperatures.

Slip and twinning, the pertinent mechanisms here, are illustrated for a simple lattice in Figure 5. Figure 5(a) represents a lattice after a given amount of slip has been completed, for the planes of atoms above and below the slip plane are in alignment. The existence of this alignment of planes after slip has occurred led originally to a theory that blocks of atoms were sliding over one another along the slip plane. However, in more recent developments based on dislocation theory, it has been recognized that it is dislocation



SLIP

(a)



TWINNING

(b)

Figure 5. Deformation mechanisms (8)
(a) slip (b) twinning

movement which causes the net movement of planes and hence deformation. For example, considering Figure 2, if the plane of atoms vertically upward from AA' were held rigid and the dislocation were permitted to move to the left, it would disappear as it passed through DD'KK' but there would be a half-plane of atoms a distance of one interatomic spacing to the left of DD'KK'. Figure 2(b) would then be similar to Figure 5(a) except that the slip distance is two interatomic distances in the latter case.

The dislocation movement and then deformation by slip is caused by the action of shear stresses on the slip plane. These stresses must be large to produce new dislocations but need not be as great if some dislocations are already present as lines of weakness in the crystal. Consequently, the more perfect or dislocation-free the crystal, the stronger the crystal is.

Twinning differs from slip in that a new configuration of atoms is generated. Actually, as shown in Figure 5(b), the twinned region is a mirror image of the untwinned portion of the lattice on the other side of a so-called twinning plane. The twins may appear as a result of heat treatment (annealing twins) or of mechanical deformation (mechanical twins). In either case, the maximum extent of the crystal deformation if by twinning alone would be only several percent; therefore, the statement is usually made that plastic deformation takes place by some combination of slip and twinning. Also, the

application of dislocation theory to twinning has not progressed to any great extent up to this time.

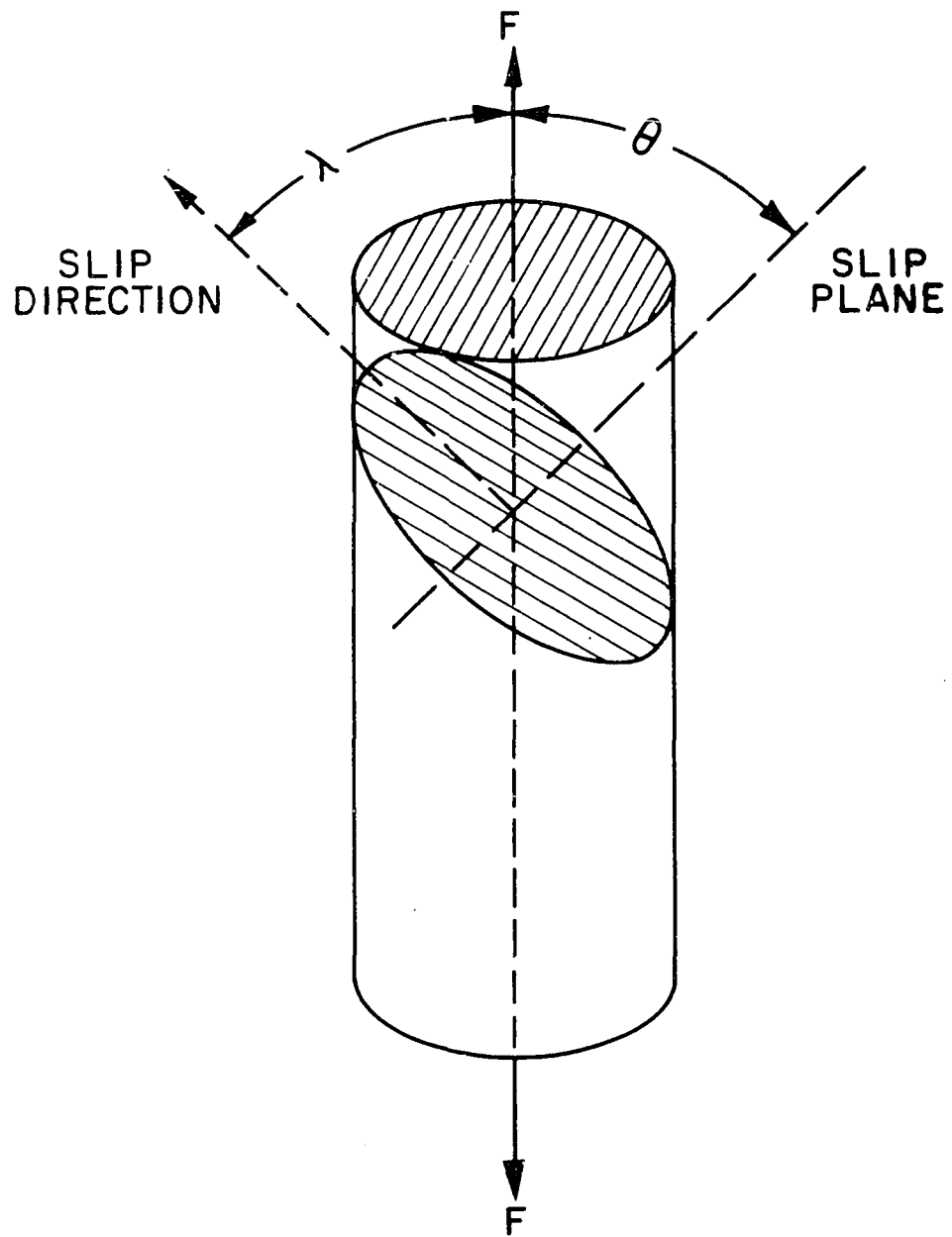
Effect of orientation Since crystals are not isotropic, the load required to cause deformation varies dependent upon the orientation of the slip plane with respect to the direction of load application. This threshold value of the shear stress for the plane is called the critical shear stress.

Resolution of the critical shear stress into a more meaningful value can be accomplished by using, for example, the cylindrical system shown in Figure 6. The stress is first corrected for the area of the slip plane based on the angle this slip plane makes with the cross section of the cylinder (equivalent to angle θ in Figure 6) yielding a stress of $(F/A) \cos \theta$. Then since certain slip directions are favored, the stress is further resolved into a component in the direction of slip by using the angle of slip or twinning described by λ . The critical resolved shear stress becomes $(F/A) \cos \theta \cos \lambda$. This value, being a resolved stress, is characteristic of the metal and the temperature.

Slip occurs most readily on the planes which have the densest packing of atoms although there will be a critical shear stress for each type of plane in the crystal. Generally, however, competition among the planes for the slip motion does not become significant except at high temperatures.

Blewitt, Coltman and Redman (3) have recently studied low

Figure 6. Significant angles in deformation of
a single crystal



temperature tensile deformation of copper single crystals and have found that the deformation of these crystals proceeds by three mechanisms: ordinary glide at low flow stresses, discontinuous slip at intermediate flow stresses, and twinning at high flow stresses for certain sample orientations. The discontinuous slip process was not noted at liquid nitrogen temperature or above; the mechanical twinning, unusual in face-centered cubic metals, was found at liquid nitrogen temperature only when the tensile orientation was near the $[111]$ direction. Essentially, these papers point out the interdependency of critical stress, orientation and temperature while the latter paper illustrates a situation where mechanism changes with temperature.

Effects of other variables The mechanical properties of single crystals are also sensitive to composition or impurity content as well as to the way in which they are handled and tested.

Atoms of an alloying element or impurity, when dissolved in the base metal, act as point defects in the lattice of the solvent. Solid solution hardening is produced in this case, and a greater effect on mechanical properties is realized than if the foreign atoms did not dissolve. Flinn (12) discussed the possible strengthening mechanisms acting here. All of the proposed explanations of the strengthening were involved with the action of dislocations as they passed through the section of the lattice which had been distorted by the presence of the

solute atom.

Thorough investigation of the influence of solute content on the mechanical properties of a crystal is complicated by the inability to obtain sufficiently accurate analyses of the crystal at the very low impurity contents involved with the high-purity metals currently available. Smith and Hendrickson (38) suggested that studies on ultra-high-purity metals should provide a better understanding of the mechanical properties of engineering materials. They commented, too, on the lack of consistent and standard analytical techniques for these composition ranges. The pertinent results from those collected in their review article, for both single crystals and polycrystalline aggregates, substantiate the claim that trace impurities are quite important in determining the strength and ductility of the material.

Machlin (26) summarized current ideas on the sensitivity of the strength properties to the characteristics of the crystal surface. From his discussion it is apparent that some attempt should be made to have control over the state of the surface and the environment of the surface during mechanical testing of single crystals. No general statements can be made for there could be either strengthening or weakening effects depending on the system.

The influence of strain rate on the results of tensile tests was discussed briefly by Malvern (27) in his survey study on single crystal plasticity. In this paper it was

shown that the stress-strain curve for a material loaded at a high strain rate lies above the curve for the same material loaded at a low strain rate. This effect was said to be very pronounced for metals such as cadmium, zinc and bismuth which tend to undergo recovery at room temperature.

Specification of crystal purity and perfection

The mechanical properties are, of course, some measure of the degree of perfection of a crystal. We have already spoken of the relationship between strength and dislocation concentration, for example. However, the evaluation procedures most frequently used are based upon physical properties of the crystal or the reaction of the crystal or specific planes of the crystal to a chemical etch.

According to Matthiessen's rule, the resistivity of reasonably pure metal is the sum of three contributing factors: resistivity due to scattering of conduction electrons by lattice vibrations and phonons (the thermal effect), resistivity due to physical defects or imperfections, and resistivity due to effect of chemical impurities in the metal. Kunzler and Wernick (21), using the assumptions that the scattering effect is negligible at liquid helium temperature and that the contribution due to physical defects would be negligible, have suggested that the resistivity at liquid helium temperature is essentially equal to the contribution from the impurities for a zone-refined ingot. These investi-

gators suggested the use of a resistivity ratio, i.e. the ratio of resistivities between liquid helium temperature and 0°C. in their case, as a means of avoiding calculation of a shape factor. They used the latter technique to determine impurity distribution along the zone-refined ingot. In their work, obviously, the resistivity ratio would increase as the purity decreased; the resistivity ratio most frequently used is the ratio, $\rho_{300^{\circ}\text{K.}} / \rho_{4.2^{\circ}\text{K.}}$

Van Bueren (44) discussed the use of resistivity data in an attempt to determine the relative amounts of impurities and imperfections by separating the influences of these types of lattice imperfections. The author suggested that measurements on quenched, irradiated, and cold-worked metals, and metals treated in more than one of these ways must be used in combination. Further, relevant data could then be obtained by observing the decrease in resistivity during annealing as defects diffuse out of material or to sinks.

The resistivity and, more particularly now, the resistivity ratio, with the latter defined usually between room temperature and liquid helium temperature, have become established as acceptable means of designating relative sample purity and, to some extent, sample perfection. More quantitative estimates of the number of dislocations present in a crystal have been made, when necessary, using etch pit density methods.

Bismuth

Bismuth is a Group V element, atomic number 83, atomic weight 209, and melting point 271°C . Bismuth crystallizes in a rhombohedral lattice in the form of two interpenetrating face-centered rhombohedral cells. Wells (45) considered the structure as one in which the (111) planes were essentially layers wherein each atom would have three close neighbor atoms at 3.10 Angstroms and three less close neighbors at 3.47 Angstroms.

Single crystals of bismuth have been grown by several investigators. For example, as previously mentioned, Kapitza (20) and Long (25) have used the Bridgman method, and Packman (32) pulled crystals of bismuth under a pressure less than 0.02 mm. Hg. The latter investigator noted that the crystals apparently grew preferentially in a direction perpendicular to the $\langle 111 \rangle$ axis. To be considered in the growth of bismuth single crystals are the facts that bismuth experiences volumetric expansion of approximately 3.32% on freezing and that the thermal conductivity of the liquid is approximately two and one-half times that of the solid.

The strength properties of bismuth have been investigated to some extent. Georgieff and Schmid (13) studied bismuth single crystals in tension and reported that elongation took place by slippage along a (111) plane in the $[10\bar{1}]$ direction. They do not mention twinning as a deformation mechanism for bismuth. Gough (15) has reported that investigation of

bismuth failed to reveal any evidence of slip when deformed at room temperature in tension, for all deformation was by the process of twinning. Gough was able to cause slip by elevating the temperature. Hall (16) reports twin components for the rhombohedral elements arsenic, antimony, and bismuth for a (011) twinning plane.

Some of the earlier investigators working with the electrical properties of bismuth reported that small traces of tin and possibly lead made the temperature coefficient of electrical resistance approximately zero at room temperature and negative at low temperature. This is a distinguishing feature of semiconductors, and probably explains the flurry of interest in bismuth in the 1930's. Thomas and Evans (42) determined some of the physical constants of lead-bismuth alloys. Some of the variables determined for the alloy series include the resistivity at 0°C., the temperature coefficient of resistance, and the thermo-electric power. The most interesting variations in these properties occurred in the region of low lead content (less than 4% by weight of lead) where curves of the property versus the weight percent bismuth have a well-defined maximum or minimum, depending on the property. The property would then change rapidly to the values for bismuth as the amount of lead is decreased.

Thompson (43) in his study of the electrical resistance of bismuth alloys, used single crystals for "consistent and interpretable results". The crystals were grown from a seed

in a vacuum. The author found the maximum in the resistivity versus composition curve just as Thomas and Evans had before him. Since he was working with single crystals, Thompson used the Voigt-Thomson law which considers crystal orientation in order to calculate the resistivities,

$$\rho_{\alpha} = \rho_{\parallel} \cos^2 \alpha + \rho_{\perp} \sin^2 \alpha$$

where ρ_{\parallel} and ρ_{\perp} are resistivities parallel to and perpendicular to the principal axis, and $\rho_{\parallel} = 138 \times 10^{-6}$ ohm cm., $\rho_{\perp} = 109 \times 10^{-6}$ ohm cm. for the 99.997% bismuth used. The testing temperature was 20°C.

Several investigators have reported values of resistivity ratios for bismuth of differing histories. From the text by Newkirk and Wernick (28), for Cerro de Pasco ingots of 99.998 - 99.999% bismuth, values of $\rho_{300^{\circ}\text{K.}}/\rho_{4.2^{\circ}\text{K.}}$ were reported as follows: initial value, 61; after 20 passes in zone refining, 673. Also, a value of $\rho_{300^{\circ}\text{K.}}/\rho_{1.5^{\circ}\text{K.}}$ of 1180 was reported. Wernick (46) reported another value of a resistance ratio, $R_{273^{\circ}\text{K.}}/R_{4.2^{\circ}\text{K.}}$, equal to 600 for zone refined bismuth. Lerner (24) obtained ratios of $\rho_{300^{\circ}\text{K.}}/\rho_{4.2^{\circ}\text{K.}}$ equal to from 120 to 200 by zone refining.

MATERIALS AND APPARATUS

Materials

Metal analyses

Bismuth Three grades of bismuth were used with compositions as shown in Table 1.

Tin Analysis of the tin used revealed a composition of 0.001% arsenic, 0.003% copper, 0.003% iron, 0.001% zinc, with the remainder tin.

Lead The lead used was nominal 4-9's grade.

Apparatus

Crystal growing unit

The basic Bridgman-type crystal growing unit used in this investigation has been completely described, except for modifications in accessories, in the report by Olson (31). A dimensional drawing of the crystallizer is shown in Figure 7, and Figure 8 is a photograph of the crystallizer plus accessories.

In this version of the Bridgman technique, there were two separately-regulated furnaces and facilities for lowering a sample, contained in a stainless steel crystallizing crucible holder, through the furnaces at a controlled rate. The crucible holder was cylindrical with removable caps at the ends. The lower end cap was fitted with a heat sink attached by a threaded shaft through a hole in the steel cap to a pedestal inside the cap. The heat sink, shaft and pedestal

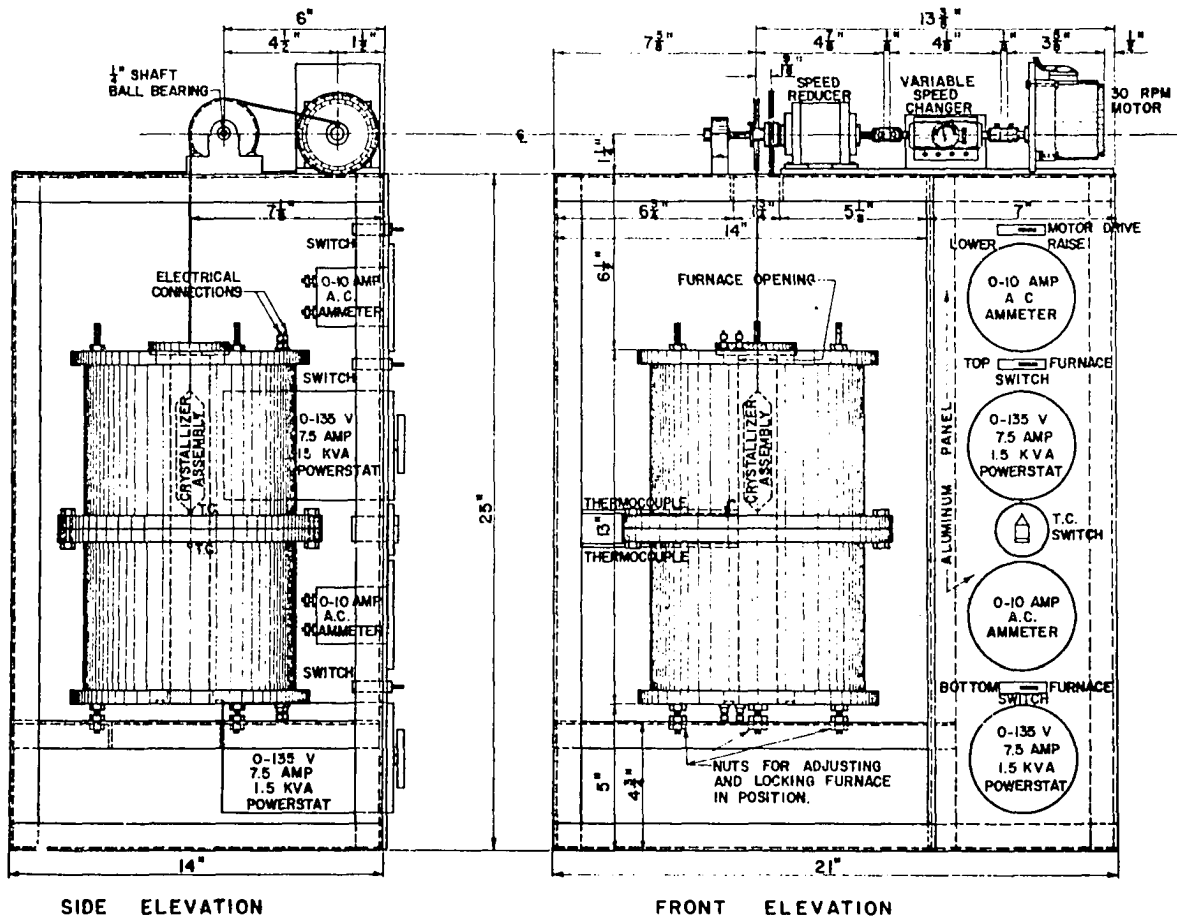
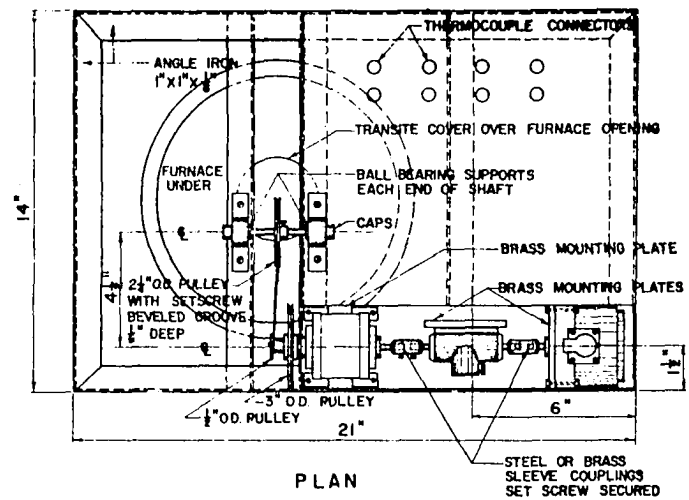
Table 1. Analysis of bismuth

Element	Grade		
	4-9's ^a	5-9's ^a	6-9's ^b
Ag	T	FT	0.1 ppm
Al	T		
Ca			0.1 ppm
Cu	T	FT-T	0.1 ppm
Fe	FT	FT	
Mg	T	FT	0.1 ppm
Ni	T		
Pb	T		0.2 ppm
Si	T	FT	0.1 ppm
% Bi (Nominal)	99.99	99.999	99.9999

^aAnalyzed by Spectrographic Group, Ames Laboratory.

^bAnalysis by vendor (Cominco Products, Spokane, Washington).

Figure 7. Dimensional drawing of Bridgman-type
crystal growing unit (31)



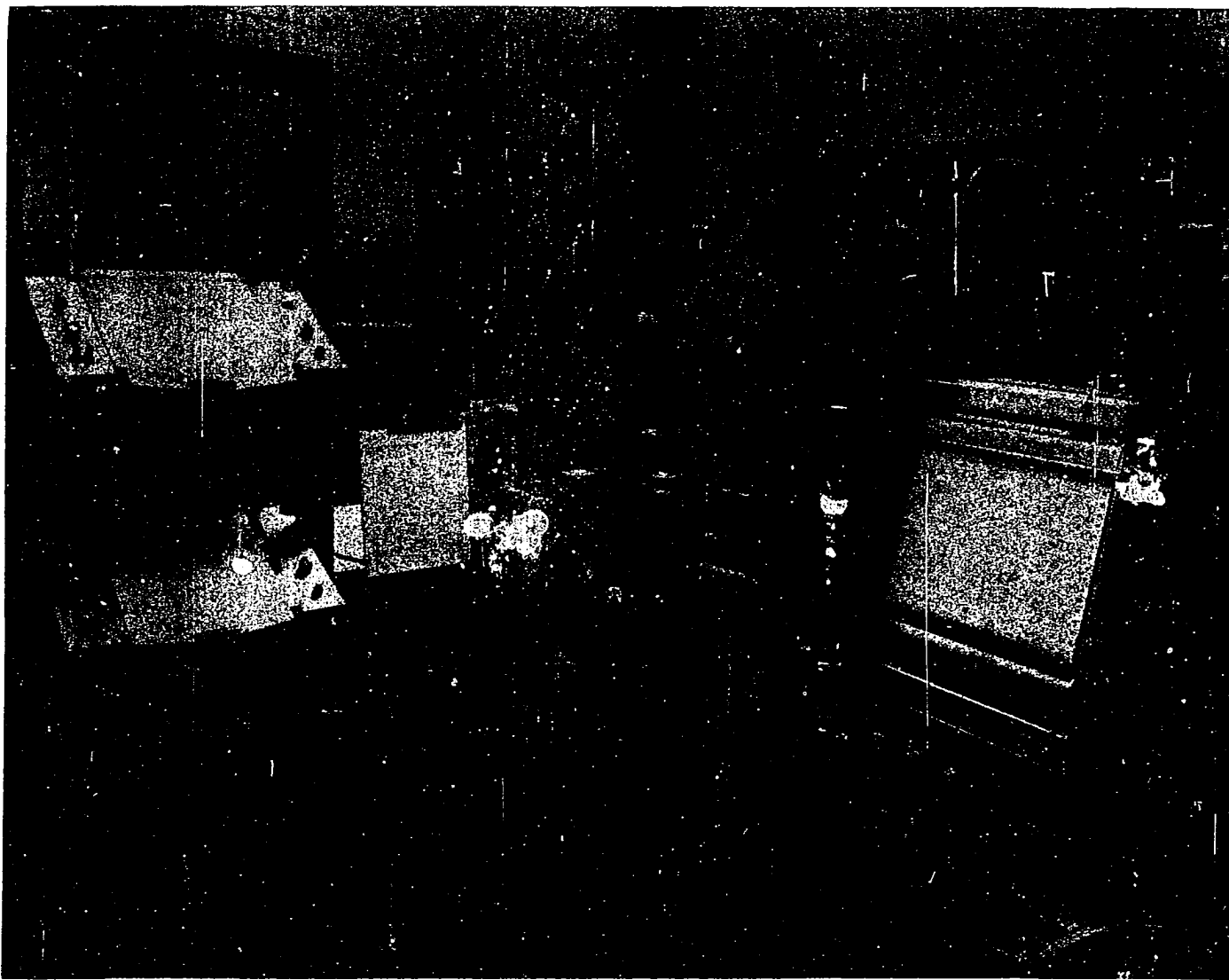


Figure 8. Bridgman-type crystal growing unit and accessories

were all of graphite and provided for rapid heat removal from the sample through the sample tip, which rested on the top of the pedestal, down into the heat sink as this assembly was lowered into the cooler region of the crystallizer furnaces.

A 22 gauge chromel wire attached to the top cap of the crucible holder was used to suspend the holder from the chain of the lowering mechanisms. A sufficient number of holes was provided in the top of the holder so that thermocouples might be inserted for temperature measurement at points along the length of the sample within the holder. Temperatures were recorded using Sargent recorders, Model MR and Model SR.

The crystallizing crucible holder is shown schematically in Figure 9. This same holder was used for all runs except those in which either an extremely fast rate of crystallization was being sought or a seed crystal was being used to produce an oriented single crystal product. The special heat sink arrangements for the latter runs are shown in Figure 10(a) and 10(b) respectively.

Casting equipment

The furnaces used for the initial casting of all specimens, both cylindrical and shaped tensile types, were regular, vertical, resistance wire wound, alundum tube furnaces 1.5 in. I.D. by 9 in. in length. Each tube carried two identical sets of resistance windings which permitted controlling the top and bottom halves of the furnaces by the use of

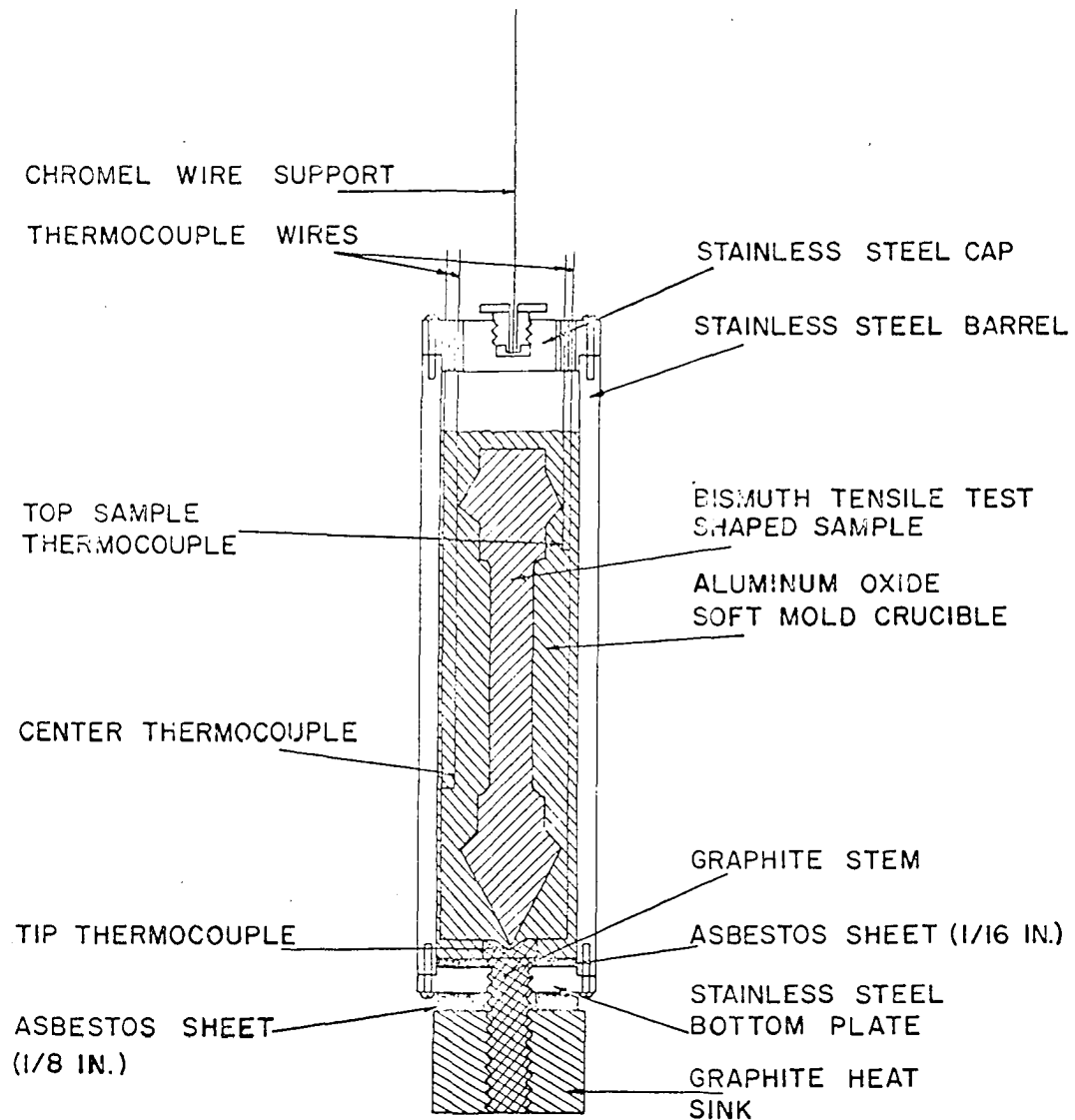
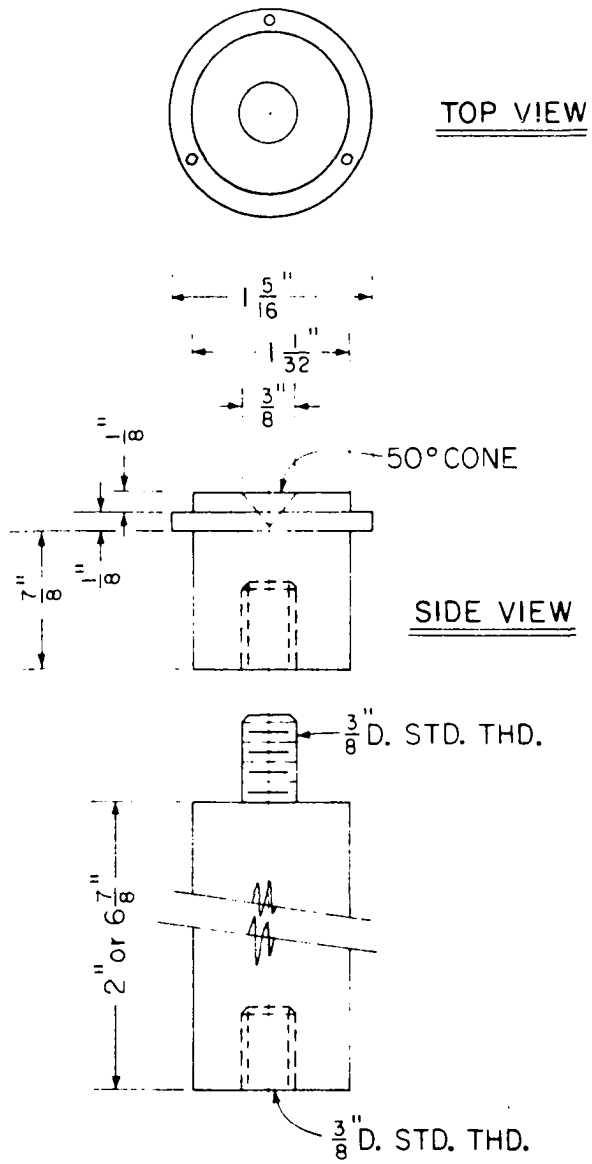
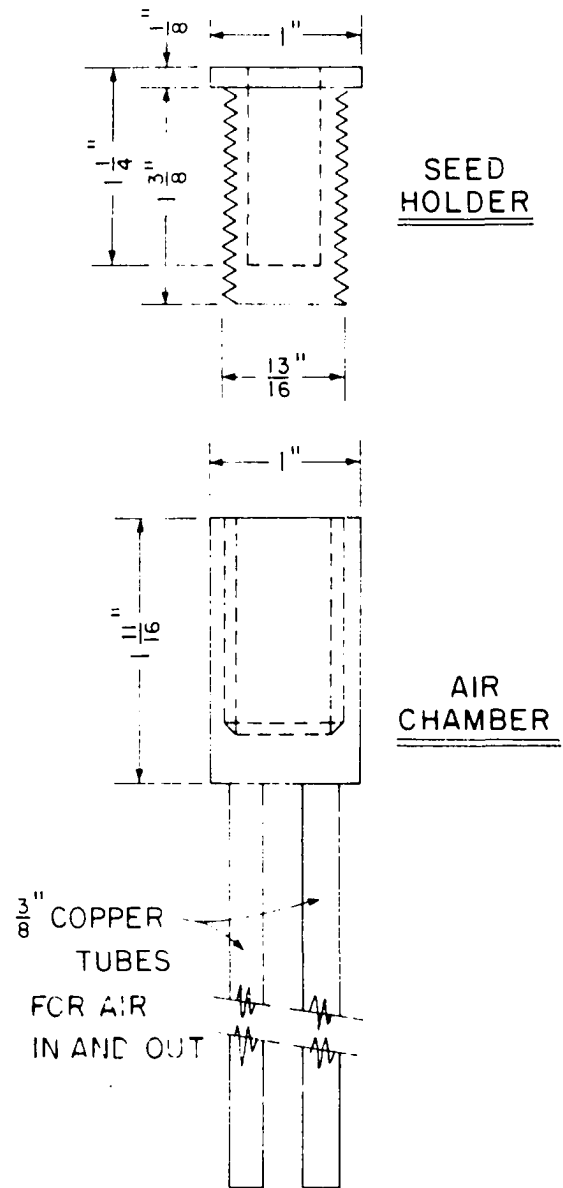


Figure 9. Crystallizing crucible unit

Figure 10. Heat sinks (a) solid copper cylinders
(b) air-cooled for oriented crystals



(a)



(b)

separate powerstats.

The molds used for casting the regular bismuth specimens were simple cylindrical graphite molds wherein the cavity dimensions varied from a 1/2 in. diameter just above the 50° conical tip to a 5/8 in. diameter at a point 3 in. higher within the mold.

Figure 11 shows the type of split mold used to cast the shaped tensile specimens. Again, a 50° conical tip was used. The important dimensions for these specimens were a gage length of approximately 1-1/2 in. and a diameter for the reduced section of approximately 5/16 in.

Equipment for testing of crystals

Tensile tests A standard Riehle testing machine was used. The loading capacity of the machine was 10,000 pounds. The range of possible rates of crosshead movement ranged from 0.002 to 2.0 in./min.

Resistivity ratios A Keithley No. 149 Millimicrovoltmeter, a standard 6-volt wet cell and a transistorized current control were used to determine the potential drop along a part of the sample length when a definite current was passed through the sample as a part of the circuit. From the potential drop at the given current, a resistance was calculated which was characteristic of the given sample at the test temperature. These determinations were performed by Dr. Douglas Finnemore and Mr. Jerome Ostenson from the

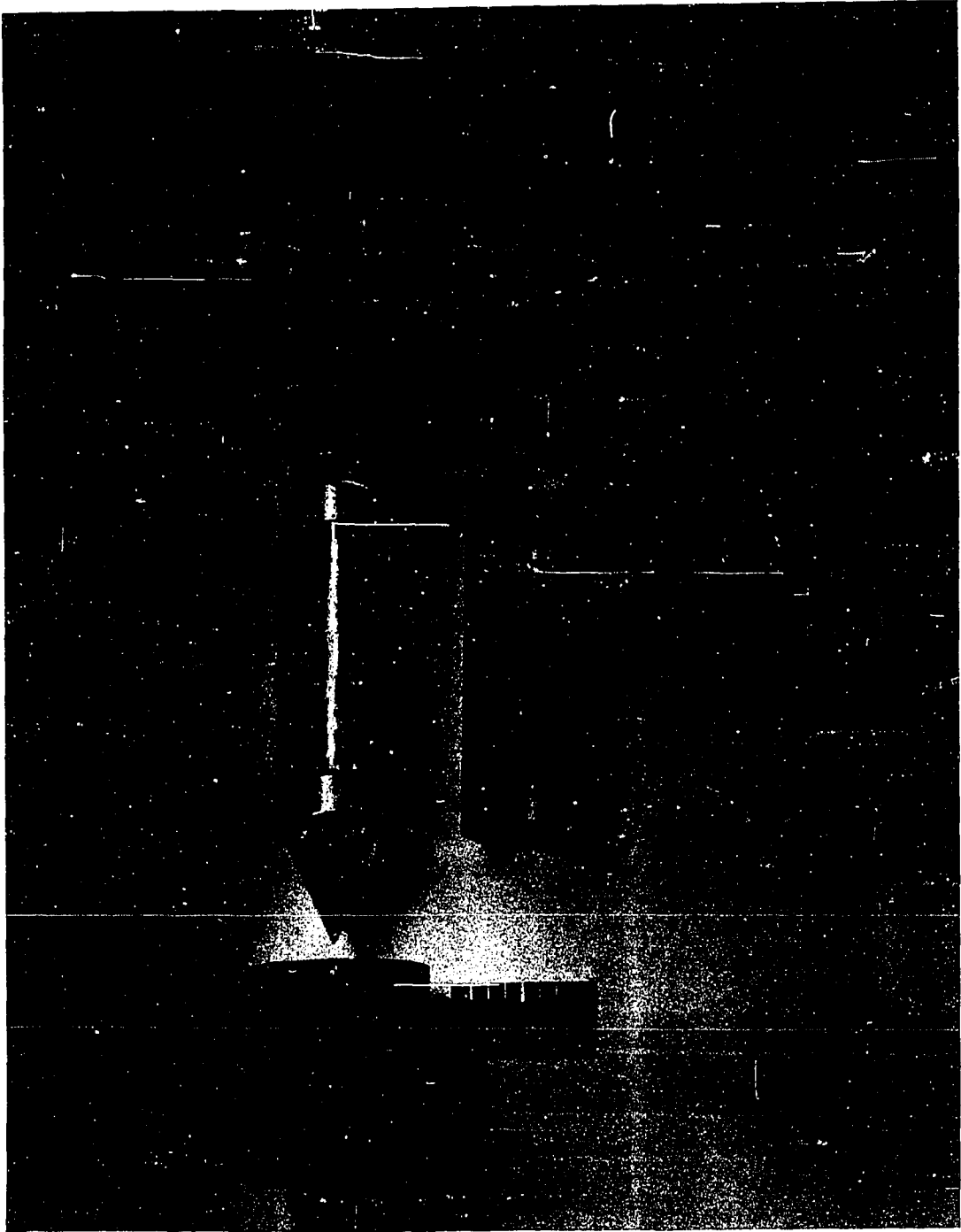


Figure 11. Split mold for casting tensile specimens

Department of Physics of the Iowa State University.

Miscellaneous analyses X-ray diffraction and spectrographic analyses were run using appropriate facilities by the respective groups at the Ames Laboratory. Messrs. Donald M. Bailey and Donald Anderson performed the x-ray analyses. Mr. Edward DeKalb performed the spectrographic analyses.

EXPERIMENTAL PROCEDURE

Preparation of Samples

Two types of samples, as shown in Figure 12, were used in this study. The same general procedure was used to prepare both sample shapes for the crystallizing runs. Polycrystalline slugs were cast in a separate furnace and were then positioned in the crystallizing crucible holder.

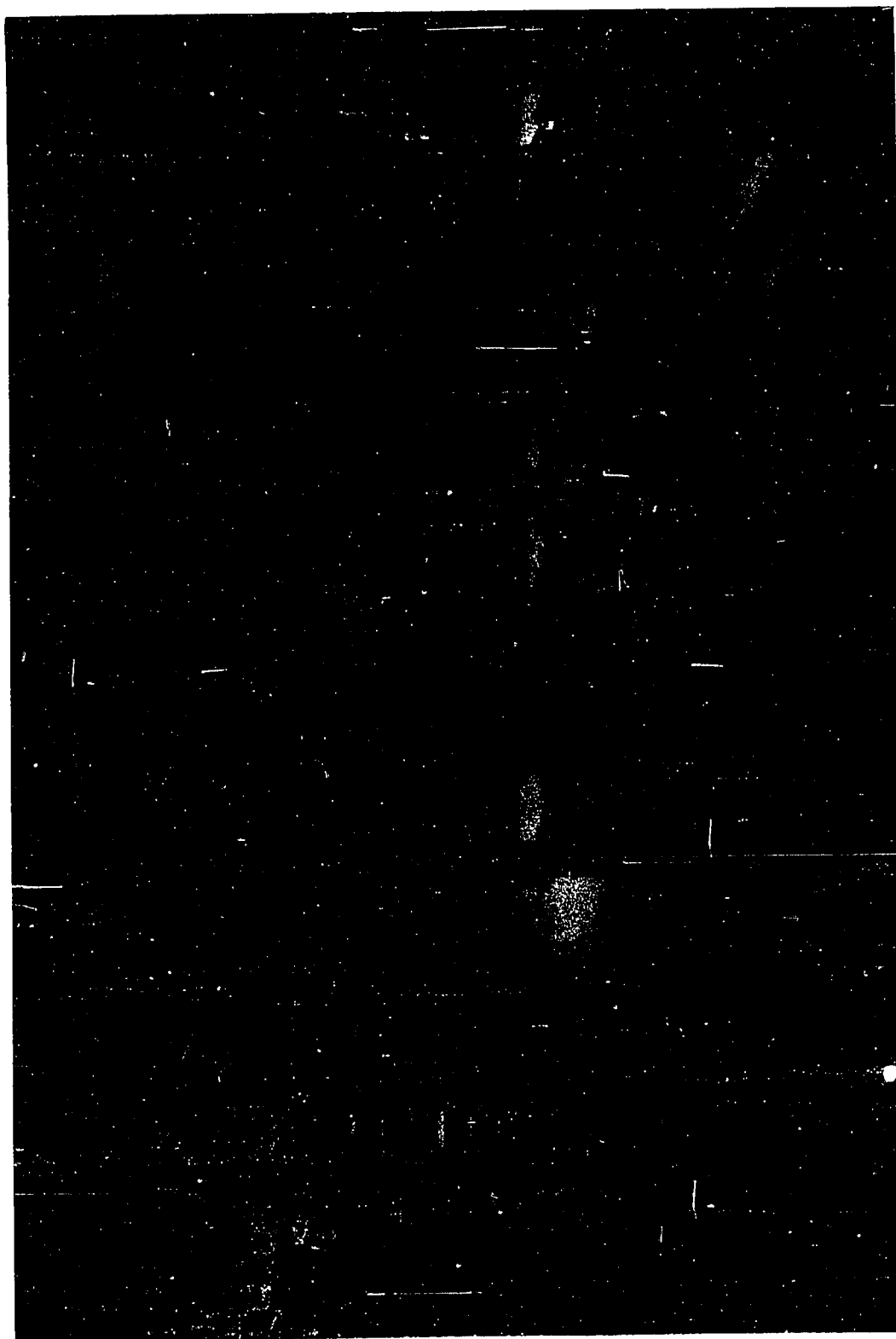
Melting and casting

The amount of bismuth required for each specimen varied from 90 to 100 grams depending upon whether a tensile specimen or a regular cylindrical specimen was being cast. The bismuth was cut into small sections, cleaned with a solution of 50 percent by volume concentrated nitric acid in distilled water, rinsed with distilled water, and air dried.

The appropriate mold was centered vertically in the casting furnace and preheated to a temperature approximately 75°C . above the melting point of bismuth. The bismuth was melted in a Pyrex test tube over an open flame and then poured directly into the mold through a small Pyrex funnel. A slow, programmed cooling procedure was followed during which the lower furnace section was always maintained at a lower temperature than the top section. By this means directional solidification of the casting, from the bottom to the top, was realized; and sound castings, free of pipes and surface cracks, were consistently obtained.

Figure 12. Typical bismuth samples
(left - regular sample: as cast and
single crystal;
right - shaped tensile specimen:
as cast and single crystal)

42b



The polycrystalline slug resulting from the casting procedure was removed from the mold, cleaned with the nitric acid solution, inspected for surface defects, rid of rough projections, and re-cleaned in preparation for the crystallizing run.

Preparation of the soft mold

The crystallizing crucible unit was prepared by first attaching the stainless steel bottom plate and the graphite stem and heat sink along with the associated asbestos washers. The thermocouple assembly and the bismuth specimen were then inserted through the open top of the barrel with the conical tip of the bismuth specimen positioned in a depression in the top of the graphite stem. Thermocouple junctions were located at the tip and at points $1\text{-}1/8$ in. and $2\text{-}7/8$ in. up from the tip. Brass wedges were used to hold the top of the specimen centered in the barrel and the specimen was held down vertically by a special clamping device.

Aluminum oxide powder (finer than 200 mesh) was poured into the crucible unit to form the soft mold around the specimen and was packed into place by action of a B.V.I. vibrator-engraver upon the outside wall of the barrel. The arrangement is shown in Figure 13. The brass wedges were removed at a time when the specimen was securely packed in place, and the top clamp was removed in time to permit the addition of sufficient powder to bring the level approximately $1/2$ in.

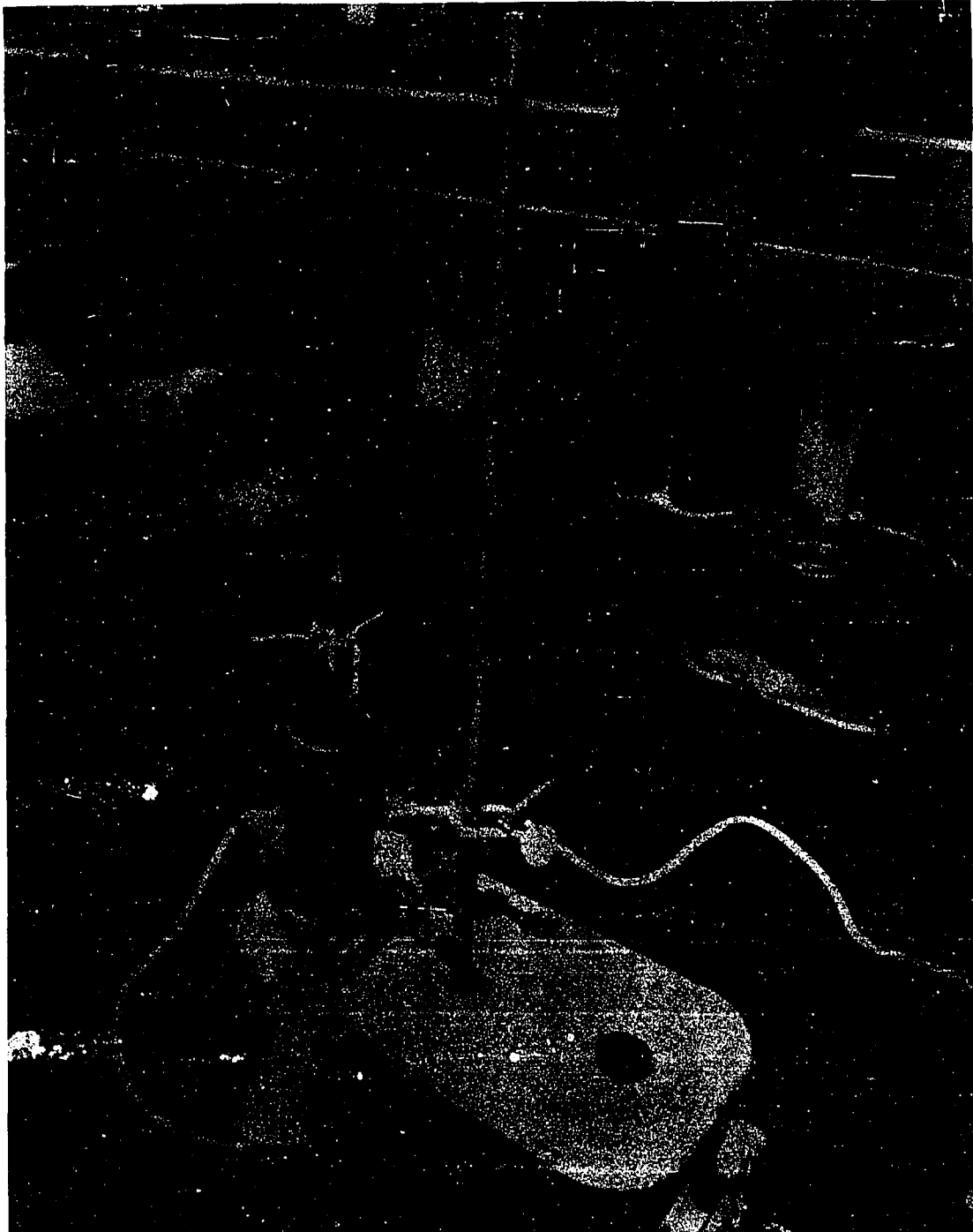


Figure 13. Packing arrangement for soft mold

above the top of the bismuth specimen.

Assembly of the crystallizing crucible unit was then completed by running the thermocouple wires out through holes in the stainless steel cap and bolting the cap in place. The thermocouple wires were electrically insulated from the unit and from each other by covering them with ceramic tubes where they came through the cap and with Variglas flexible insulation outside of the crucible unit. The crucible unit was then suspended using the chromel support wire from the stainless steel bead chain which was a part of the sample lowering assembly.

For the runs in which oriented single crystals were grown, the special bottom plate and heat sink shown in Figure 10 were used. The single crystal seed with the proper crystallographic orientation and with a size of approximately $1/4$ in. by $1/4$ in. by 1 in. was positioned on top of a fourth thermocouple junction located on the inside bottom of the well in the graphite heat sink. Aluminum oxide powder was packed around the seed. At this time the bottom plate and heat sink were attached to the barrel of the crystallizing unit, and preparations continued as before. In these runs, the conical tip of the polycrystalline slug rested on top of the seed crystal in direct contact with it.

Growing of Single Crystals

Standard procedure

The procedure for growing a crystal in the Bridgman unit consisted essentially of three steps: heating the sample above its melting point, holding the sample above its melting point long enough to destroy any growth nuclei which might exist in the melt, and then lowering the sample at a predetermined rate into the cooler region of the unit so that the nucleus could form and grow from the tip of the crucible to the top of the melt.

In the usual runs for this investigation, the crystallizing crucible unit was positioned during heat-up with the heat sink extending into the lower, cooler furnace so that melting of the slug from the top down could be assured. Specifically, the top of the unit was placed 2-3/4 in. down from the transite top of the furnace. Power to the furnaces was turned on and the sample heated until the temperature at the top of the sample was approximately 310-320°C. At this point the crucible unit was raised completely into the top furnace. Heating was continued until the sample tip temperature reached a temperature of approximately 340°C. and the sample top temperature was no greater than approximately 430°C. The power to the furnaces was then reduced, and the system was stabilized at a point where specimen tip and top temperatures were approximately 300°C. and 320°C. respectively.

Once steady-state conditions had been realized, the actual lowering of this crucible unit into the cooler furnace was started. The unit was lowered at a predetermined rate for a total distance of approximately 6 in. At this time all power to the furnaces and to the lowering assembly was shut off, and the sample was cooled to near room temperature in the furnace. Then, the crystallizing crucible unit was removed from the furnace and disconnected from the lowering mechanism. The top of the unit was opened, and the sample was carefully removed from the unit by first slowly pouring out the aluminum oxide powder.

The bismuth specimen resulting from the crystallizing run was then etched with the solution of 50 percent by volume concentrated nitric acid in distilled water, rinsed, and air dried. Visual inspection revealed whether or not a single crystal had been obtained.

Procedure for oriented single crystals

The procedure for growing the oriented single crystals was similar to that for the regular samples except for the precautions taken to prevent the seed from melting completely along its length. Specifically, the well in the special heat sink shown in Figure 10(b) was designed to permit use of a seed with a long dimension vertically. Also, facilities were provided for air cooling of the lower end of the heat sink and thus one end of the seed. Since the seed could not be seen,

temperatures obtained from thermocouples at both the upper and lower ends of the seed were used continuously to estimate the amount of the seed which was molten.

The crucible unit was again positioned during heat-up with the heat sink extending into the lower, cooler furnace. The unit was raised into the upper furnace after the top of the specimen had melted. The system was then brought to thermal equilibrium by the same procedure as before, except that air was being continuously supplied from the laboratory air lines through a rotameter to the air chamber of the heat sink. Typical steady-state temperatures obtained at the lower tip of the seed, at the junction between the top of the seed and the tip of the slug, and at the lower and upper ends of the reduced (in diameter) section of the specimen were in the order of 225, 290, 380 and 400°C. respectively.

The flow of air to the heat sink was gradually reduced as the crucible unit was lowered into the cooler furnace, and outside cooling became unnecessary.

At the end of these runs, after the specimen had cooled to near room temperature and the crucible unit had been removed from the furnace and disconnected from the lowering mechanism, both the top and the bottom of the unit were opened. The crystal and seed were then both removed, examined to confirm contact, etched with the nitric acid solution, rinsed and air dried. A visual inspection of the specimen and

the seed revealed whether or not these were single crystals. Orientation of the (111) cleavage plane of the specimen relative to that for the seed was checked by actual cleaving of the samples at liquid nitrogen temperature. This latter examination was accomplished after other tests on the specimen had been completed.

DISCUSSION OF RESULTS

A total of 73 crystallizing runs were made: 43 runs for the shaped tensile test specimens of bismuth and 30 runs with more widely varying conditions for the regular cylindrical specimens. The results of these runs are shown in Tables 2 through 7.

The first three of these tables contain the data on the shaped tensile specimens with randomly oriented cleavage planes. For these runs, no attempt was made to control the plane orientation. Only the composition and, indirectly, the crystallization rate were used as controllable variables; and all other conditions were kept essentially constant for every run. The data show the complete randomness of the orientation of the cleavage plane with respect to the major axis of the crystal. Specifically, for example, with one group of tensile crystals, values of the orientation angle θ from 13° to 81° have occurred all at approximately the same growth rate.

With regard to this effect, theory says only that the perfect crystal is difficult to grow except in directions perpendicular to loosely-packed planes and will not occur easily in a direction perpendicular to closely-packed planes unless dislocations are present (6). There is some thought that anisotropy of thermal conductivity can influence crystal orientation by causing a tendency for directionality of heat

Table 2. Data on shaped tensile test specimens - 99.99% bismuth

Sample No. and Class () Bi4-TS-	Length reduced section in.	Diameter reduced section in.	Lowering rate in./min.	Cryst. rate in./min.	θ	γ	α	Yield or twinning load.lb. (Strain rate-0.02 in./min.)	CRSS kg./mm ²	CRTS kg./mm ²
1 (S)	1.50	0.310	0.00560		53	8.5		Y 25.0	0.110	
2 (S)	1.54	0.305	0.00583	0.0109	65	27	16	T-Y79.8 ^a	0.261	0.122
3 (A)	1.60	0.320	0.00582	0.00950	71	39.5	50	T 43.5	0.0900	0.192
4 (A)	1.57	0.314	0.00463	0.00666	74.2	18	41	T 22.0 ^b	0.0496	0.0985
5 (P)	1.57	0.317	0.00571	0.0150	85					
6 (S)	1.56	0.315	0.00580	0.00818	81.5	58	18	T 80.0	0.0557	0.207
7 (S)	1.57	0.314	0.0150	0.0171	86	24	34	T 68.5	0.0394	0.289
8 (A)	1.56	0.317	0.0148	0.0257	81	10	39	T 30.0	0.0405	0.130
9 (S)	1.56	0.316	0.0147	0.0300	85	34	36.5	T46.1	0.0296	0.197
10 (A)	1.57	0.317	0.0147	0.0230	32	60		Y 61.0	0.122	
11 (P)	1.56	0.315	0.0147	0.0237	50					
12 (A)	1.58	0.314	0.0119	0.0228	42	36		Y 46.0	0.167	
13 (A)	1.56	0.315	0.0119	0.0185	28	33	28	Y-T55.2	0.172	0.206
14 (S)	1.57	0.310	0.00971	0.0180	80	46	24.5	T55.5	0.0550	0.195

Table 2 (Continued).

Sample No. and Class()	Length reduced section in.	Diameter reduced section in.	Lowering rate in./min.	Cryst. rate in./min.	θ	γ	α	Yield or twinning load.lb.	CRSS kg./mm. ²	CRTS kg./mm. ²
Bi4-TS-								(Strain rate-0.02 in./min.)		
15 (A)	1.44	0.317	0.00974	0.0200	49	22		Y 34.2	0.139	
16 (P)	1.57	0.315	0.0131	0.0240	46					

^aPerhaps some twinning first.

^bPoor specimen alignment during test.

Legend for Class:

- (S) - single crystal
- (A) - acceptable for test
- (P) - polycrystalline

Table 3. Data on shaped tensile test specimens - 99.999% bismuth

Sample No. and Class()	Length reduced section in.	Diameter reduced section in.	Lowering rate in./min.	Cryst. rate in./min.	θ	γ	α	Yield or twinning load.lb.	CRSS kg./mm. ²	CRTS kg./mm. ²
Bi5-TS-								(Strain rate-0.02 in./min.)		
1 (S)	1.56	0.312	0.00589	0.0106	59	9		Y 24.5	0.0979	
2 (A)	1.60	0.310	0.00582	0.0190	81	21	20	T 36.5	0.0489	0.109
3 (P)	1.55	0.310	0.00545							
4 (P)	1.57	0.310 ^a	0.00579	0.0109						
5 (P)	1.56	0.311	0.00578	0.0100	47					
6 (S)	1.60	0.313	0.00588	0.00856	70	31	50	T 52.0	0.130	0.233
7 (S)	1.50	0.318	0.00582	0.00856	13	51		Y 81.0	0.0985	
8 (A)	1.55	0.317	0.0155	0.0211	56	18		Y 81.0	0.317	
9 (S)	1.57	0.314	0.0148	0.0277	68	45		Y 52.5	0.117	
10 (A)	1.56	0.315	0.0147	0.0225	82	8	45	T 50 ^b	0.0613	0.225
11 (S)	1.56	0.315	0.0148	0.0257	87	1	25	T 55.0	0.0259	0.190
12 (P)	1.56 ^a	0.310 ^a	0.0146							

^aApproximate dimension.

^bEstimate - chart disfigured.

Legend for Class:

(S) - single crystal
 (A) - acceptable for test
 (P) - polycrystalline

Table 4. Data on shaped tensile test specimens - 99.9999% bismuth

Sample No. and Class()	Length reduced section in.	Diameter reduced section in.	Lowering rate in./min.	Cryst. rate in./min.	θ	γ	α	Yield or twinning load.lb.	CRSS kg./mm ²	CRTS kg./mm ²
Bi6-TS-								(Strain rate-0.02 in./min.)		
1 (S)	1.55	0.318	0.0148	0.0237	31	3		Y 48.1	0.187	
2 (A)	1.55	0.319	0.0149	0.0200	70	3	47	T 90.5	0.279	0.395
3 (S)	1.40	0.319	0.0149	0.0237	67	32		Y 69.0	0.184	
4 (S)	1.56	0.315	0.00580	0.00796	35.5	42		Y 43.6	0.138	
5 (P)	1.54	0.317	0.00580		78.5					
6 (S)	1.59	0.320	0.00589	0.0100	45	26		Y 37.8	0.148	
7 (A)	1.53	0.318	0.00597	0.00833	38	2		Y 66.5 ^a	0.284	
8 (P)	1.51	0.317	0.0146		45.5					
9 (S)	1.52	0.317	0.00589	0.00963	68.5	7		Y 62.0 ^a	0.187	
10 (A)	1.52	0.318	0.0147	0.0225	65.5	35.5	13	T 108.0 ^a	0.293	0.209
11 (A)	1.52	0.315	0.0148	0.0250	64.5	2		Y 64.0	0.223	
12 (A)	1.56	0.317	0.0143	0.0257	55.8	46		(special test)		
13 (S)	1.53	0.319	0.0145	0.0234	34	56		(special test)		

Table 4 (Continued).

Sample No. and Class()	Length reduced section in.	Diameter reduced section in.	Lowering rate in./min.	Cryst. rate in./min.	θ	γ	α	Yield or twinning load.lb. (Strain rate-0.02 in./min.)	CRSS kg./mm. ²	CRTS kg./mm. ²
Bi6-TS-										
14 (S)	1.63	0.317	0.0144	0.0231	73.5	51	27	T 54.0	0.0821	0.193
15 (S)	1.50	0.315	0.00592	0.00984	30	50.5		Y 82.0	0.203	

^aStrain rate - 0.10 in./min.

Legend for Class:

- (S) - single crystal
- (A) - acceptable for test
- (P) - polycrystalline

removal from crystals during formation (18). According to this reasoning, there should be an even greater tendency toward large values of ϕ at fast lowering rates than at slow lowering rates.

Since composition and growth rate were the significant variables in the crystallization runs for these tensile specimens, the tabulated data shows the relative importance of these variables with respect to the probability of successful growth of a single crystal. For the 4-9's, 5-9's and 6-9's bismuth, the percent of the runs resulting in single crystals were 37.5%, 41.7%, and 53.3% respectively; the percent of the runs resulting in samples acceptable for testing were 81.3%, 67.7% and 86.7% respectively. Of the 19 single crystal tensile specimens grown, ten were from runs at low rates of crystallization and nine were from runs at the higher crystallization rates. Over-all, 41.2% of the acceptable specimens were grown at low rates, the remaining 58.8% at fast rates. Therefore, over the established, relatively wide range of operating conditions, material purity has a definite effect on the ease with which a single crystal is produced.

Tables 2 to 4 also show the relative strength properties of the shaped single crystal test specimens. One of the earliest effects noticed during the tensile testing of these specimens was the obvious difference in behavior of the crystals during the tests dependent upon the orientation of the crystal lattice relative to the direction of loading.

Figures 14 through 16 show typical examples of stress-strain diagrams which resulted from the tests and illustrate the change from deformation by slip for crystals with small values of ϕ to deformation by twinning for crystals with large ϕ , where ϕ is actually the angle between the normal to the true cleavage plane and the major axis of the single crystal grown. The transition from slip to twinning as the predominant deformation mechanism has been estimated from this experimental data as being approximately where ϕ equals 70° .

Georgieff and Schmid (13) define the (111) plane as the important slip surface for bismuth single crystals. This surface is said to act as the cleavage plane of the nonductile, large ϕ crystals and at lower temperatures it becomes the cleavage surface of the ductile, low ϕ crystals. The specific (111) plane meant here is the "well-defined" or pseudo-octahedral plane which is described using the fundamental rhombohedron and which should be distinguished from the three, less well-defined planes which are equivalent to each other and which are each at an angle of $71^\circ 37.5'$ from the (111) cleavage and/or slip plane.

In this study, the (111) plane was determined for each sample by cleaving an undisturbed section of the sample after all testing had been completed. The section was first cooled in liquid nitrogen and then struck a sharp blow with a sharp tool. The characteristic $[\bar{1}10]$ slip direction was then determined by means of a Laue x-ray photograph taken

Figure 14. Stress-strain diagram for sample with
small Θ

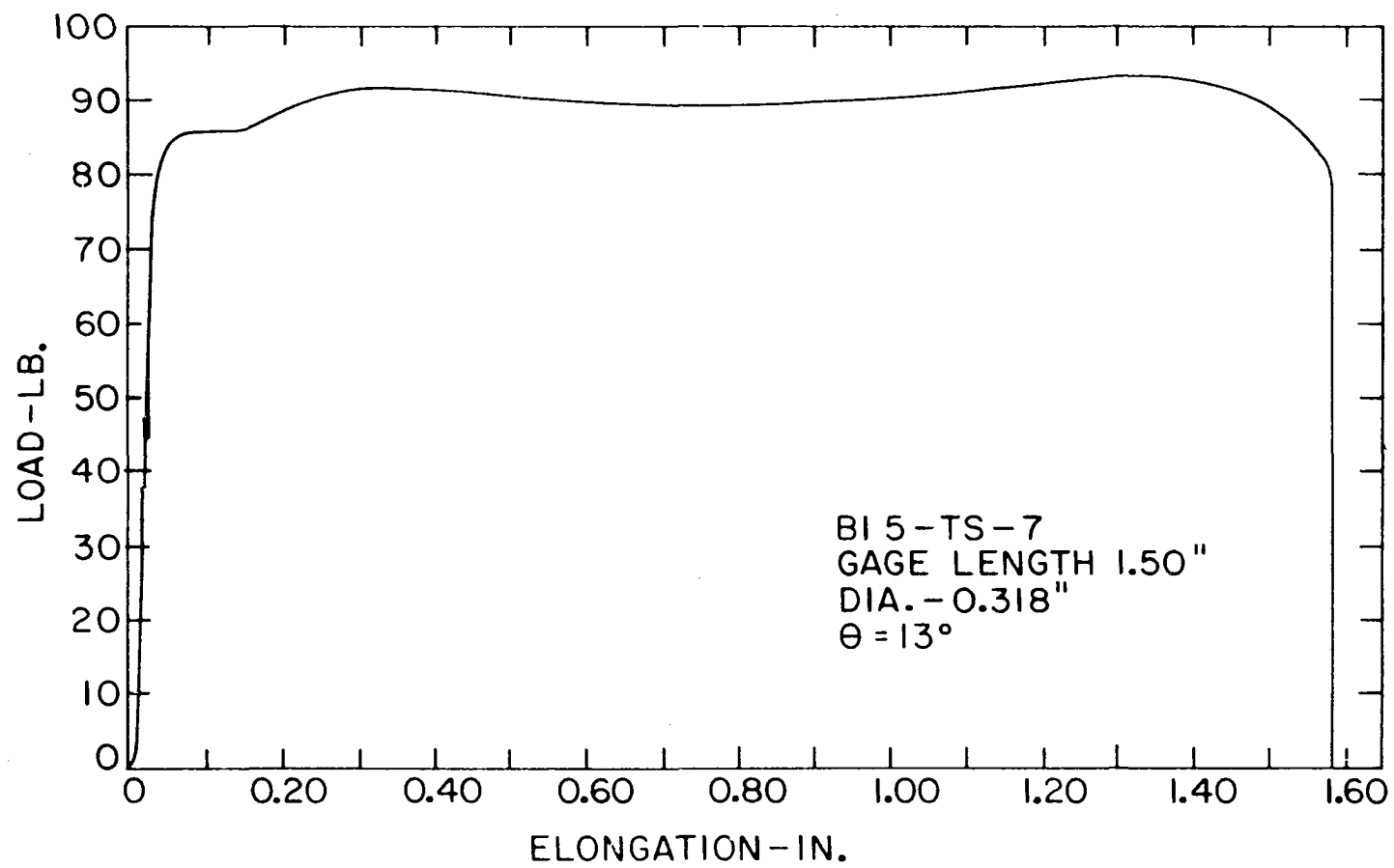


Figure 15. Stress-strain diagram for sample
with intermediate θ

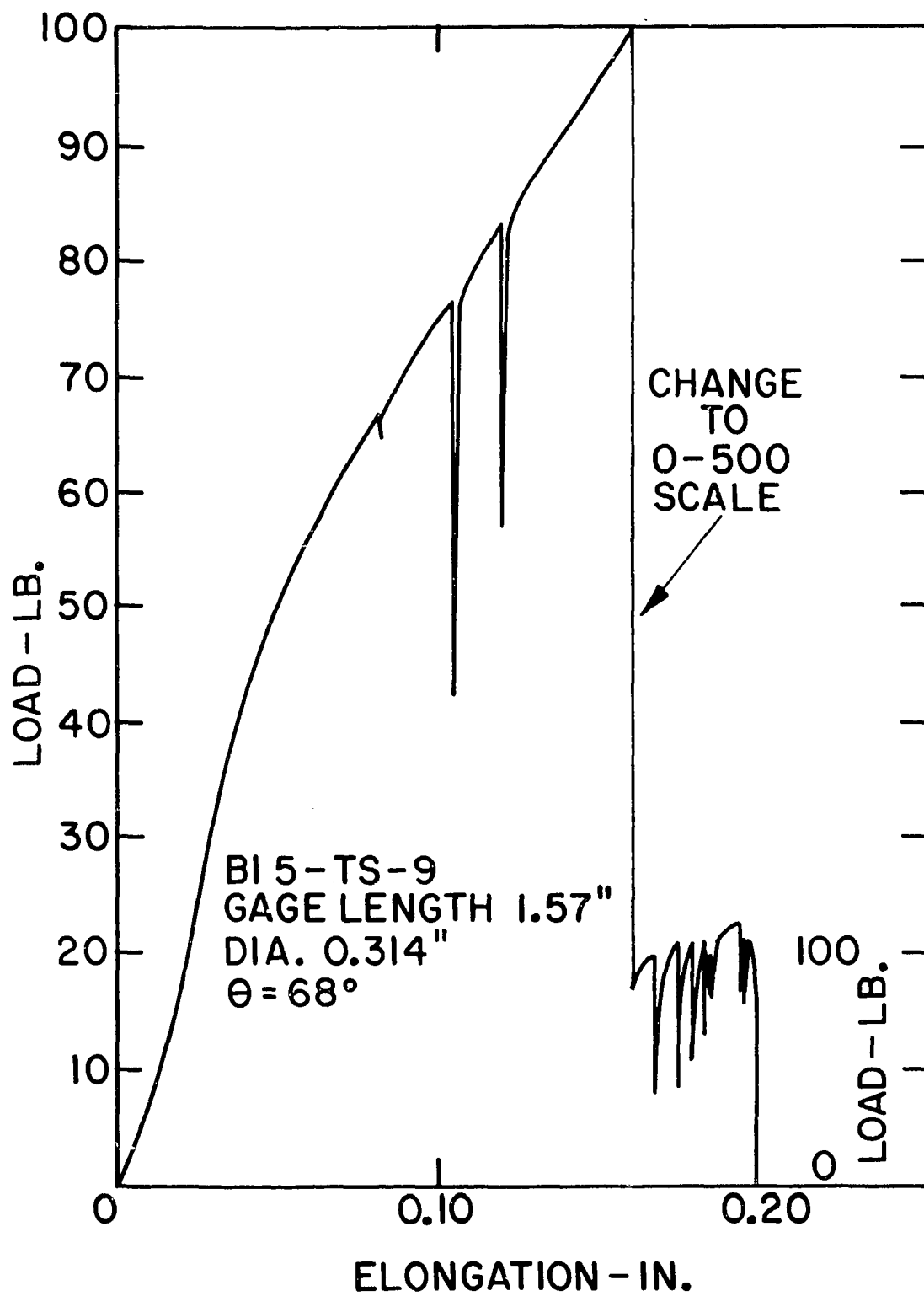
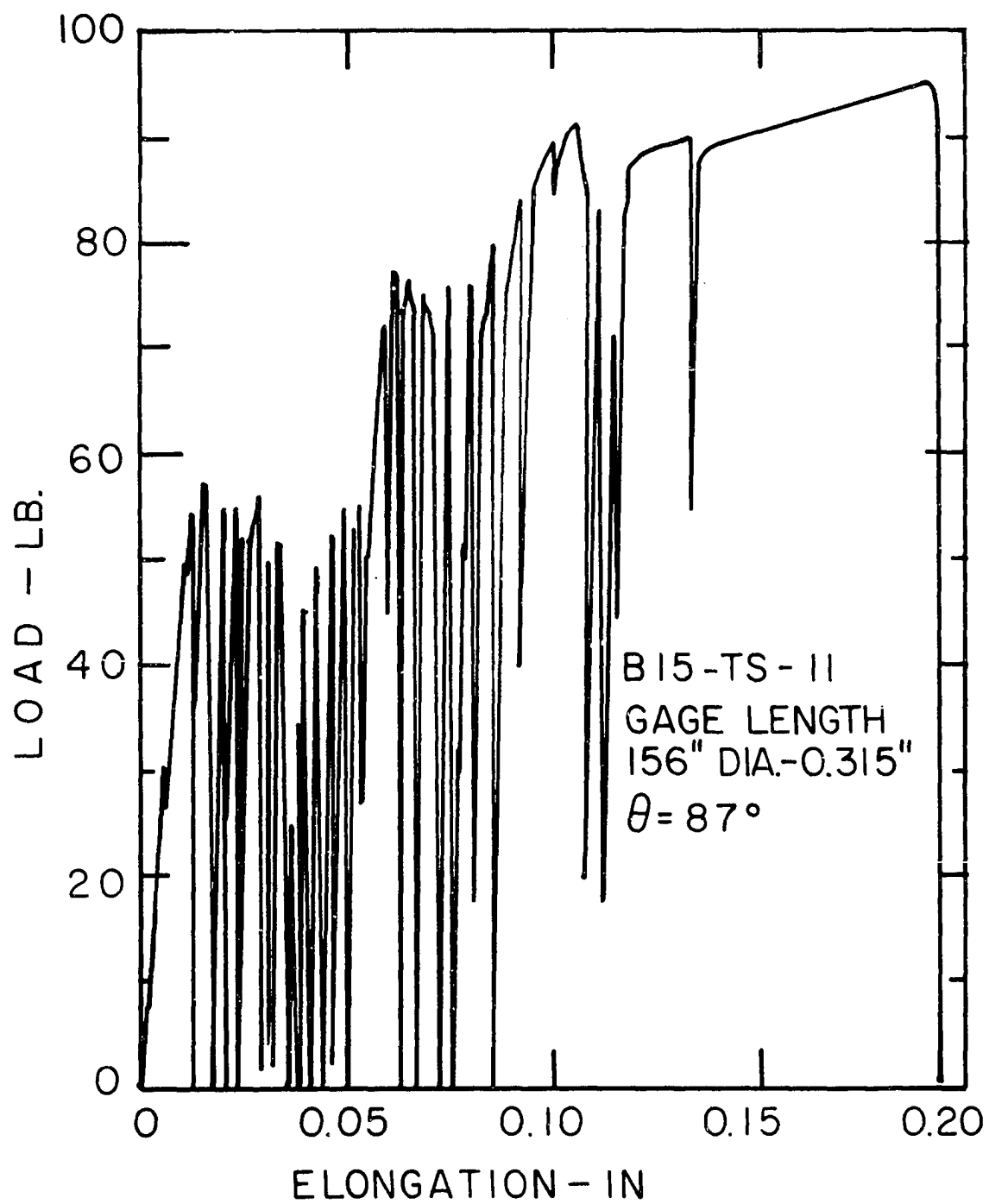


Figure 16. Stress-strain diagram for sample
with large Θ



perpendicular to the cleaved (111) surface.

As previously mentioned, the change from ductile to brittle behavior as a function of the angle θ apparently takes place at a value of θ equal to approximately 70° based on the experimental data. Georgieff and Schmid (13) have said that if the angle between the slip plane and the direction of loading of the sample is greater than $55^\circ 42'$ the crystal is "non-ductile"; crystals with this angle less than $55^\circ 42'$ behave in a ductile manner. It is believed that these investigators considered one of the less well-defined (111) planes in their analysis; for if the $71^\circ 37.5'$ angle between these planes and the (111) cleavage and slip surface is taken into consideration, the calculated, equivalent value of θ , as defined here, is $74^\circ 4.5'$ which is close to the estimated value of 70° .

The critical resolved shear stress (CRSS) was calculated for each specimen by first using the angle θ to resolve the force on to the (111) plane and to correct the area factor from the cross-sectional area to that of the actual slip or shear plane in the sample. Then the angle γ between the slip direction and the major axis of the slip plane was used to resolve the force in the (111) plane to the $[\bar{1}10]$ direction. The resulting equation for the critical resolved shear stress was

$$\text{CRSS} = \frac{F}{A} \sin \theta \cos \gamma \cos \phi$$

which is equivalent to the relationship

$$\text{CRSS} = \frac{F}{A} \cos \theta \cos \lambda$$

mentioned earlier. Although values of this quantity were calculated and are listed for all specimens, the significant values are those for samples which deformed first by slip and for which the familiar yield point could be defined on a stress-strain diagram. Average values of the critical resolved shear stress for samples of this type at a strain rate of 0.02 in./min. are: for the 4-9's bismuth, 0.135 kg./mm.²; 5-9's bismuth, 0.105 kg./mm.²; and for the 6-9's bismuth, 0.181 kg./mm.². These compare with the accepted value of 0.221 kg./mm.² for approximately 3-9's bismuth.

A closer examination of the resolved stress values reveals that, for each purity tested, as the rate of crystallization was increased there was an increase in the critical resolved shear stress. This increase can most probably be explained by an increase in the dislocation concentration or an increase in the number of vacancies "quenched" into the crystal at the higher growth rates.

For the specimens tested which deformed first by twinning, a form of critical resolved twinning stress was calculated. The twinning components for bismuth are the (110) plane and the $[00\bar{1}]$ direction in that plane (16). The actual plane

involved in the twinning action was readily visible on the sample surface as was the formation of the twin bands during the test. In order to define the resolved twinning stress, the force was resolved onto the plane defined by the twin band and the area corrected to that of the twinning plane. The direction of twinning was assumed to be along the major axis of the twinning plane. Therefore, if α is defined as the angle between the twinning plane and the direction of load application, the critical resolved twinning stress becomes:

$$\text{CRTS} = \frac{F}{A} \cos \alpha \sin \alpha$$

The average values of this quantity at a strain rate of 0.02 in./min. are: for the 4-9's bismuth, 0.202 kg./mm.²; for the 5-9's bismuth, 0.189 kg./mm.²; and for the 6-9's bismuth, 0.294 kg./mm.²

From Tables 2 to 4 it can be seen that these values are not as influenced by composition as are the resolved shear stresses, for there is more overlapping of the individual experimental values between the several grades of bismuth used.

Tables 5 to 7 include data on the high and low temperature resistivities of the cylindrical specimens and the resistance or resistivity ratios for these products of crystallization runs with the three grades of bismuth. In analyzing the data, that for the single crystals is emphasized, and the effect of crystal lattice orientation on the resistivity is not considered. However, it can be seen that in the usual case,

Table 5. Data on cylindrical specimens - 99.99% bismuth

Sample No.	Heat sink	Lowering rate in./min.	Cryst. rate in./min.	ϕ	Resistivities ohm-cm. $\times 10^6$ 300°K. 4.2°K.		$\rho_{300}/\rho_{4.2}$	Description of product
Bi-4-1	Graphite	0.0155	- ^a	90	121	6.81	17.8	Single
Bi-4-2	Graphite	0.00550	0.00690					Bi-crystal
Bi-4-3	Graphite	0.00561	0.00980	30.5	131	4.84	27.1	Single
Bi-4-4	8" Cu	0.179						4-5 crystals
Bi-4-5	3-1/8" Cu	0.178	0.193	85	149	5.20	28.7	Single
Bi-4-6	8" Cu	0.177	0.138		123	6.91	17.8	2-3 crystals
Bi-4-7	8" Cu	0.0845	0.0967	43.5	134	6.41	20.9	Single
Bi-4-8	8" Cu	0.0263	0.0257	43	147	7.57	19.4	Bi-crystal
Bi-4-9	8" Cu	0.00581	0.00645	55	138	4.99	27.7	Single
Bi-4-10	Graphite	0.0142	0.0168	19.5	149	5.60	26.6	Bi-crystal
Bi-4-11	Graphite	0.00594	0.00807	16.2	154	6.81	22.6	Single
Average of single crystals:					138	5.85	24.0	

^aSample thermocouple shorted out.

Table 6. Data on cylindrical specimens - 99.999% bismuth

Sample No.	Heat sink	Lowering rate in./min.	Cryst. rate in./min.	ϕ	Resistivities ohm-cm. $\times 10^6$ 300°K. 4.2°K.		$\rho_{300}/\rho_{4.2}$	Description of product
Bi-5-C				46	148	0.742	200	As cast - single
Bi-5-1	Graphite	0.0155	0.0264	67.4	123	0.605	203	Single
Bi-5-2	Graphite	0.00561	0.00982	78	118	0.480	246	Single
Bi-5-3	3-1/8" Cu	0.177	0.171	37.5	122	0.747	164	Single
Bi-5-4	8" Cu	0.129	0.107	74	131	0.752	174	2-3 crystals
Bi-5-5	(Suspension chain broken)							
Bi-5-6	8" Cu	0.0562	0.0528	78	124	0.792	156	Single + fleck near top
Bi-5-7	8" Cu	0.0098	0.0107		142	0.802	177	Polycrystal
Bi-5-8	8" Cu	0.0272	0.0264	90	122	1.04	117	Single + fleck near top
Bi-5-9	8" Cu	0.00581	0.00623	89	124	0.420	295	Single
Bi-5-10	Graphite	0.0143	0.0161	42.5	141	0.716	197	Bi-crystal
Bi-5-11	Graphite	0.00592	0.00817	75	126	0.38	332	Single
Average of single crystals:					123	0.638	216	

Table 7. Data on cylindrical specimens - 99.9999% bismuth

Sample No.	Heat sink	Lowering rate in./min.	Cryst. rate in./min.	Ø	Resistivities ohm-cm. x 10 ⁶ 300°K. 4.2°K.		$\rho_{300}/\rho_{4.2}$	Description of product
Bi-6-1	Graphite	0.0149	0.0172	74.5	127	0.580	219	Single
Bi-6-2	Graphite	0.00580	0.00674	64.8	131	0.494	265	Single
Bi-6-3	Graphite	0.0149	0.0188	42.7	141	0.807	175	Single + flecks and striations
Bi-6-4	Graphite	0.0149	0.0193		134	1.00	134	Polycrystal
Bi-6-5	3-1/8" Cu	0.172	0.193	86.5	152	0.338	450	Single above conical tip
Bi-6-6	8" Cu	0.172	0.153	87.5	127	0.383	332	Single + flecks in tip
Bi-6-7	Graphite	0.00577	0.00798	58.5	142	0.510	278	Single + flecks
Bi-6-8	Graphite	0.0138	0.0168	89.5	130	0.353	368	Single + flecks
Average of single crystals:					136	0.495	298	

even for the products described as polycrystalline, the resistivity data are not radically influenced by the presence of grain boundaries to the extent that they exist here. Also, the use of resistivity ratios minimizes geometric effects.

The usual crystallization procedures were followed for these groups of specimens, but an effort was made to increase the range of crystallization rates. Through the use of copper heat sinks and a rapid lowering rate in some runs, heat was extracted from the specimen tip more quickly than in the usual crystallization runs. Specifically, average crystallization rates as high as 0.193 in./min. were realized along approximately three inches of the 1/2 in. diameter cylindrical specimens. These rates are compared to the rates on the order of 0.0065 to 0.025 in./min. used normally for these specimens.

The important variable with these samples again was sample purity. The resistivity and resistivity ratio data follow Matthiessen's rule fairly well in this regard. The high temperature resistivity is little affected by the range of composition and crystallization conditions described in Tables 5 to 7; but the low temperature resistivity and, of course, the resistivity ratio are mainly influenced by purity and only slightly influenced by the rate of crystallization.

The data of Table 8 briefly illustrate the effect of more extreme differences of physical perfection on specimens of a given purity. In the first two samples, a change in grain size and perhaps a decrease in internal stresses caused no

Table 8. Data on miscellaneous specimens - 99.9999% bismuth

Sample description and treatment	Resistances ohm x 10 ⁶		Resistivities ohm-cm. x 10 ⁶		$\rho_{300}/\rho_{4.2}$
	300°K.	4.2°K.	300°K.	4.2°K.	
1. As received from vendor, fine-grained	318	10.6			30.0
2. As received from vendor, annealed 6 hours at 244°C., then 6 hours at 264°C. Larger grain size than when received	332	5.1			65.0
3. As received from vendor, melted in Pyrex test tube and cast in graphite crucible	262	1.77	132	0.893	148
4. Single crystal No. Bi-6-1, shock-loaded	258	2.24	130	1.13	115
5. Shaped tensile test specimen Bi6-TS-12					
(a) Single crystal, as crystallized	600	2.61	120	0.523	229
(b) 0.15 in. strain at 0.02 in./min.	665	26.75	133	5.36	24.8
(c) 0.35 in. additional strain (0.50 in. total) at 0.02 in./min.	763	71.5	153	14.3	10.8
6. Shaped tensile test specimen Bi6-TS-13					
(a) Single crystal, as crystallized	680	3.40	138	0.69	200
(b) 0.15 in. strain at 0.10 in./min.	690	27.85	140	5.65	24.8
(c) 0.35 in. additional strain (0.50 in. total) at 0.10 in./min.	813	74.0	165	15.0	11.0

significant change in the high-temperature resistance but decreased the low-temperature resistance by a factor of two, thereby increasing the resistivity ratio. Resistances were used here directly because of the irregular sample shape.

From combined data of Tables 7 and 8, it can be seen that a cast slug, a single crystal, and a shock-loaded single crystal, all of the same material, have essentially the same high-temperature resistivity. However, the low-temperature resistivity is lowest for the single crystal and highest for the shock-loaded crystal; the resistivity ratio undergoes the corresponding inverse changes in magnitude. The data on specimens Bi6-TS-12 and Bi6-TS-13 in Table 8 show a similar relative sensitivity of the low-temperature resistivity for specimens deformed in tension at two different strain rates. The latter crystals were both ductile with ϕ less than 70° .

Some impurity tests were made wherein small amounts of lead or tin were added to either 5-9's or 6-9's bismuth, and samples were cast in the same size and shape as the regular cylindrical samples using clean, graphite molds. A qualitative spectrographic analysis of typical cast alloys revealed good distribution of the added element throughout the castings. Specifically, 0.25%, 0.50% and 0.75% of each element were added to separate samples and low- and high-temperature resistance measurements were run.

Pertinent data from the tests described are shown in Table 9 and illustrate the relative effects of added elements

Table 9. Effects of alloying on resistivity ratios

Sample No.	Impurity added	Percent impurity (by weight)	Resistivities ohms cm. x 10 ⁶ $\rho_{300}/\rho_{4.2}$		
			300°K.	4.2°K.	
Base metal 99.999% bismuth:					
Bi5-IT-2c	4-9's Bi	50	138	3.96	34.8
Bi5-IT-5c	4-9's Pb	0.50	192	- ^a	
Bi5-IT-6c	4-9's Pb	0.25	172	- ^a	
Bi5-IT-9c	4-9's Pb	0.75	227	- ^a	
Bi5-IT-10c	4-9's Sn	0.50	361	32.9	10.9
Bi5-IT-12c	4-9's Sn	0.25	283	25.0	11.3
Bi5-IT-14c	4-9's Sn	0.75	431	42.4	10.2
Base metal 99.9999% bismuth:					
Bi6-IT-1c	4-9's Sn	0.25	320	27.2	11.8
Bi6-IT-2c	4-9's Sn	0.50	398	38.3	10.4
Bi6-IT-3c	4-9's Sn	0.75	417	43.9	9.5

^aLow-temperature resistances inconsistent with lead as added element.

on the resistivities and the resistivity ratio. It will be noted that no success was realized in measuring resistances at 4.2°K. for bismuth-lead alloys, presumably because of the superconductivity effects demonstrated by lead at these low temperatures. Where measurements were possible, it became quite obvious that in this range of concentrations both low- and high-temperature resistivities were affected by the added element. The increase in the low-temperature resistivity is relatively greater than that of the high-temperature resistivity, so that the net result is a decrease in resistivity ratio with an increase in the amount of added element.

The attempts to grow single crystals with a controlled lattice orientation did not meet with immediate success. A problem of maintaining contact between clean surfaces of the single crystal seed and the cast slug was readily solved so that the crystallographic orientation of the seed was maintained as crystallization proceeded. However, because of the basic nature of bismuth, which has a low recrystallization temperature, any significant handling of the seed resulted in the formation of extra crystals within the seed during heating and frequently changed the orientation of the product. Also, some difficulty was met initially by the inability to maintain a slow rate of crystallization and still retain a sufficiently low seed tip temperature.

The problem of recrystallization was minimized by taking extreme care in handling the seed and by cutting the seeds

using a spark cutting procedure. The rate of heat loss from the sample was decreased by constructing the seed holder section of the heat sink from stainless steel instead of graphite. The lower thermal conductivity of the steel permitted better control of the temperature gradient across the seed and, therefore, better control of the rate of crystallization.

Table 10 contains data on representative samples from the two extreme cases within this group: crystals with the (111) cleavage plane either perpendicular to or parallel to the growth axis of the crystal. The successful growth of these samples also provided an opportunity for studying the tensile behavior of such crystals. Critical resolved shear stresses are tabulated for all samples. However, although here again some glide may precede the twinning action in the samples with large θ , the critical resolved twinning stresses are felt to be most meaningful.

Similarly, for the samples with small θ wherein the (111) cleavage planes are essentially perpendicular to the growth axis, the resolved load is approaching zero and a critical normal stress is more significant for correlation purposes. This value is defined by the equation:

$$CNS = \frac{F}{A} \sin^2 \phi$$

where ϕ is the angle between the (111) plane and the growth axis.

Table 10. Single crystal tensile test specimens with controlled orientation of growth axis

Sample No.	Cryst. rate in./min.	θ	α	ϕ	Yield or twinning load.lb.	CRSS kg./mm. ²	CRTS kg./mm. ²	CNS kg./mm. ²
(Strain rate - 0.02 in./min.)								
Bi5-OTS-21	0.00677	86	37		T 70.5	0.0430	0.302	
Bi5-OTS-22	0.00968	88	39		T 56.8	0.0177	0.248	
Bi5-OTS-23	0.00578	84	39		T 26.2	0.0243	0.114	
Bi5-OTS-24	0.00434	5	50	85	Y 68.2	0.0529		0.602
Bi5-OTS-26	0.00630	1	53	89	Y 73.0	0.0113		0.648
Bi5-OTS-28	0.00585	1	57	89	Y107	0.0166		0.952

CONCLUSIONS

Growth and Properties of Bismuth Single Crystals

Growth of single crystals

1. It is possible to grow single crystals of bismuth in the shape of tensile test specimens consistently by using the Bridgman procedure and a soft mold technique. The shaped crystals grown had a test section approximately $5/16$ in. in diameter and a gage length of $1-1/2$ in. with an overall length of approximately $3-1/2$ in.
2. Shaped single crystals of bismuth can be grown over a range of operating conditions. Average crystallization rates estimated at from 0.00666 to 0.030 in./min. along the test section were used with success in this study. In tests with regular, cylindrical specimens of approximately $1/2$ in. diameter, average crystallization rates as high as 0.193 in./min. were found to be satisfactory.
3. Within the ranges of operating conditions used, material purity has a definite and perhaps dominant influence on the probability of success in growing a single crystal.
4. The rate of crystallization of the crystals grown has no apparent effect on the orientation of the crystal lattice with respect to the direction of growth.
5. Shaped bismuth single crystals with predetermined lattice

orientations can be grown using a single crystal seed and the Bridgman technique. Crystals have been grown with the (111) cleavage planes oriented either perpendicular to or parallel to the direction of growth.

Properties of single crystals

Mechanical properties

1. Bismuth single crystals with the angle θ between the normal to the (111) cleavage plane and the direction of tensile loading less than approximately 70° exhibit ductile behavior in a tensile test and apparently deform by the slip mechanism. Crystals with θ greater than 70° are brittle and apparently deform predominantly by the twinning mechanism.
2. The critical resolved shear stress of the single crystals grown is mainly a function of the material composition. At a strain rate of 0.02 in./min., the average values of this variable for the grades of bismuth used are: for the nominal 4-9's bismuth, 0.135 kg./mm.^2 ; for the 5-9's bismuth, 0.105 kg./mm.^2 ; for the 6-9's bismuth, 0.181 kg./mm.^2 .
3. For each of the three grades of bismuth used, an increase in the rate of crystallization causes an increase in the critical resolved shear stress of the resultant crystals.

4. Although bismuth is known to experience recovery at room temperature, an increase in strain rate does cause an increase in the critical resolved shear stress.
5. A critical resolved twinning stress can be calculated for those crystals in which the first significant permanent deformation is by twinning. This quantity is numerically larger than the critical resolved shear stress and is not as sensitive to composition as is the latter variable. At a strain rate of 0.02 in./min. the average values of this variable for the grades of bismuth used are: for the 4-9's bismuth, 0.202 kg./mm^2 ; for the 5-9's bismuth, 0.189 kg./mm^2 ; and for the 6-9's bismuth, 0.294 kg./mm^2 .

Electrical properties

1. Resistivity ratios ($\rho_{300^\circ\text{K.}}/\rho_{4.2^\circ\text{K.}}$) for the bismuth single crystals grown and tested vary as a function of crystal purity with the ratios of resistivities between 300°K. and 4.2°K. for the 4-9's bismuth crystals averaging 24.4, those for the 5-9's averaging 191 and those for the 6-9's averaging 298.
2. For the range of compositions from 99.99% bismuth to 99.9999% bismuth inclusive, no significant variation exists in the 300°K. resistivities of similar single crystals. However, the resistivities at 4.2°K. decrease

with increasing purity to yield the significant change in the resistance or resistivity ratios ($\rho_{300^{\circ}\text{K.}}/\rho_{4.2^{\circ}\text{K.}}$) with the change in composition.

3. For a given crystal purity, no apparent correlation exists between the resistivity ratio and the orientation angle, θ , for the crystal.
4. For a given crystal purity, there is a slight increase in resistivity ratio with a decrease in the rate of crystallization.
5. The resistivity ratio for a fine-grained polycrystalline sample can be increased by annealing to cause grain growth in the sample. The increase in resistivity ratio is caused by a decrease in the resistance at 4.2°K. ; the 300°K. resistance remains substantially constant.
6. As an "impurity" element is added to bismuth, within the composition limits of the solid solubility of that element in bismuth, the resistivities at both 300°K. and 4.2°K. increase. The low-temperature value increases more rapidly relative to the 300°K. value, thus causing a significant decrease in the resistance or resistivity ratio.
7. As stress is introduced into a bismuth single crystal, the resistivity at both 300°K. and 4.2°K. increases. The low

temperature value increases more rapidly relative to the 300°K. value, thus causing a decrease in the resistance or resistivity ratio.

8. For a single crystal experiencing deformation in tension, the resistivity ratio is influenced by the amount of strain but is little affected by the rate of straining.

SUMMARY

The purpose of this investigation was to study some of the factors affecting the growth and the mechanical and physical properties of bismuth single crystals. The rate of crystallization and sample purity were of primary interest as variables in the crystallization runs. Crystal lattice orientation, crystal perfection and the testing conditions themselves were considered as variables in some of the studies of crystal properties. Three grades of bismuth were used containing 99.99%, 99.999% and 99.9999% bismuth respectively.

Two types of crystals were grown using the Bridgman procedure and a "soft mold" technique. Shaped specimens for tensile testing had a gage length of approximately 1-1/2 in. and a diameter of approximately 5/16 in. for this reduced section. Tapered cylindrical specimens, with the diameter varying from 1/2 in. to 5/8 in. over a 3 in. length, were used for tests other than tensile tests. In both cases, the bismuth was first cast in an appropriate graphite mold and was solidified directionally from a 50° conical tip using a programmed cooling procedure. The shaped polycrystalline slug was then packed in the "soft mold" of alundum powder within a stainless steel crystallizing crucible, and the crystallizing run was executed. Also, a method was developed and is presented for growing single crystals of desired crystallographic orientation again using the Bridgman method

but with a single crystal seed. This procedure was used to grow the shaped tensile specimens with primary cleavage planes oriented either parallel to or perpendicular to the growth axis.

Randomly oriented single crystals were successfully produced with crystallization rates of from 0.00666 to 0.030 in./min. along the reduced section of the tensile specimens and to as high as 0.193 in./min. along the cylindrical specimens. It was apparently easier to grow single crystals as the material purity increased. Also, within these limits the critical resolved shear stress was greater and the resistivity ratio was less for crystals grown with the faster crystallization rates. No apparent correlation existed between crystallization rate and the orientation of the crystal lattice with the direction of crystal growth.

Resistivity ratios between 300°K. and 4.2°K. for the cylindrical single crystals averaged 24.4, 191 and 298 for the 4-9's, 5-9's and 6-9's bismuth respectively. The 300°K. resistivities were essentially the same for the three grades of bismuth studied with the 4.2°K. resistivities reflecting the effects of impurities or imperfections. Addition of alloying elements up to a maximum of 1.0% caused both low- and high-temperature resistivities to increase, the former more rapidly than the latter.

The behavior of the single crystals during tensile testing was dependent on the angle between the primary cleavage plane

and the direction of load application. If the angle between the normal to this plane and the load direction was less than 70° , the crystal behaved in a ductile manner and slip was predominant; if the angle was greater than 70° , brittle behavior and twinning were predominant. The critical resolved shear stresses and critical resolved twinning stresses calculated were reasonably consistent and were sensitive to both strain rate and crystal purity.

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ACKNOWLEDGMENTS

The author wishes to express his appreciation to all those who were so helpful during the course of this investigation. Acknowledgment is made of the assistance of the Graduate Committee: Drs. Morton Smutz, John F. Smith, Lawrence E. Burkhart, Maurice Larson and George Burnet. Also, individuals from the departments of Chemical Engineering, Metallurgy and Physics and from the Ames Laboratory staff cooperated most readily in various stages of the investigation.

Particular mention is made of three people without whose combined efforts the work would not have progressed so smoothly or so pleasantly: Dr. Morton Smutz, for his advice, cooperation and continued inspiration; Mr. Edwin H. Olson, for his concerned interest and consistent helpfulness; and Mr. Harvey Jensen, for his many contributions and for the conscientious use of his skills.

Finally, the author wishes to gratefully acknowledge the assistance of his wife, who has offered him constant encouragement and who has so ably typed and helped to assemble this thesis.

APPENDIX

Nomenclature

Letters

A	cross sectional area of sample, mm^2
CNS	critical normal stress, kg./mm^2
CRSS	critical resolved shear stress, kg./mm^2
CRTS	critical resolved twinning stress, kg./mm^2
F	load in tension, lb.
FT	in qualitative spectrographic analysis, faint trace quantities of an element
R	resistance, ohm
T	identification for tension load at yield point when twinning is predominant; or, in qualitative spectrographic analysis, trace quantities of an element
Y	identification for tension load at yield point when slip is predominant

Greek symbols

α	angle between twinning plane and direction of load application, degrees
γ	angle between direction of slip and the major axis of the elliptical (111) primary cleavage plane, degrees
θ	angle between the normal to the (111) primary cleavage plane and the direction of load application, or angle between the sample axis and the "c" axis of the rhombohedral crystal, degrees
λ	angle between direction of slip and direction of load application, degrees
ρ	resistivity, ohm cm.
ϕ	angle between (111) primary cleavage plane and direction of load application, degrees